REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
30-06-2013	Final Report	1-Aug-2005 - 30-Sep-2011

4. TITLE AND SUBTITLE
MRFM MURI ARO Final Report

5a. CONTRACT NUMBER
W911NF-05-1-0403

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHORS
John Sidles, John Marohn, Al Hero

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Washington
Office of Sponsored Programs
4333 Brooklyn Ave NE
Seattle, WA 98195 -9472

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
48082-MS-MUR.1

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
The goal of this MURI was to detect magnetic resonance from an individual proton using magnetic resonance force microscopy (MRFM). Pushing MRFM to single-proton sensitivity requires meeting three experimental challenges: (1) Fabricating nanomagnets which produce a large magnetic field gradient and yet have only a thin damage layer, (2) Understanding and mitigating the large non-contact friction (and frequency noise) typically experienced by an attonewton-sensitivity cantilever near a surface, and (3) Devising a suitable spin detection protocol.

15. SUBJECT TERMS
MRFM, Nuclear, Spin, DNP, Cantilever, nanomagnets, imaging,

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		John Sidles
					19b. TELEPHONE NUMBER
					206-522-7513

Report Title

MRFM MURI ARO Final Report

ABSTRACT

The goal of this MURI was to detect magnetic resonance from an individual proton using magnetic resonance force microscopy (MRFM). Pushing MRFM to single-proton sensitivity requires meeting three experimental challenges: (1) Fabricating nanomagnets which produce a large magnetic field gradient and yet have only a thin damage layer, (2) Understanding and mitigating the large non-contact friction (and frequency noise) typically experienced by an attonewton-sensitivity cantilever near a surface, and (3) Devising a suitable spin detection protocol.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. J. A. Marohn, Using Cantilevers to Probe Carrier Diffusion and the Electronic Energy Levels of Charged Defects in Films of Organic Semiconductors, Materials Research Society Fall Meeting; Boston, Massachusetts; November 26 – 30, 2012, [url].

2. J. A. Marohn, Charting a path to 1 nm resolution magnetic resonance imaging of biomacromolecules: High-gradient magnet-tipped cantilevers and dynamic nuclear polarization in magnetic resonance force microscopy, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, [url].

3. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, Development and characterization of high-gradient cobalt-tipped cantilevers, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, [url].

4. R. Picone, J. Garbini, and J. A. Sidles, Separatory Magnetic Transport in Magnetic Resonance Force Microscopy, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, 2012, [url].

5. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient cobalt nanomagnets integrated on attonewtonsensitivity cantilevers for scanned probe magnetic resonance detection of nuclear spins, Gordon Research Conference on Nanostructure Fabrication; Biddeford, Maine; July 15 – 20, 2012, [url].

6. J. A. Marohn, Using cantilevers to detect magnetic resonance, spectroscopically probe electronic energy levels, and image charge generation at the nanoscale, Cornell Center for Materials Research Symposium, Next-Generation Materials Characterization; Ithaca, New York; May 22, 2012, [url].

7. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. Rettner, D. Rugar, and J. A. Marohn, Nanofabrication of magnet-tipped, high gradient cantilevers for scanned probe nano-MRI, First Quadrennial Juniata College Chemistry Alumni Symposium; Huntingdon, Pennsylvania; April 13 – 14, 2012.

8. J. A. Marohn, Towards Nanometer Resolution Single Particle Imaging by Mechanically Detected Magnetic Resonance, The Scripps Research Institute; La Jolla, California; January 4, 2012.

9. J. A. Marohn, Discussion Leader, Electron and Nuclear Spins (Part 1), Gordon Research Conference on Magnetic Resonance; Biddeford, Maine; June 12 – 17, 2011, [url].

10. J. G. Longenecker, Electron spin resonance detection of nitroxide labels by magnetic resonance force microscopy, Gordon Research Seminar on Magnetic Resonance; Biddeford, Maine; June 11 – 12, 2011.

11. J. A. Marohn, Mechanically Detected Magnetic Resonance from TEMPAMINE and the Feasibility of Imaging Single-Spin EPR from such a Workhorse Spin Probe, Session on Frontiers of Electron Paramagnetic Resonance in Biological and Inorganic Materials; Eastern Analytical Symposium; Somerset, New Jersey; November 14 – 17, 2011.

12. J. A. Sidles, Transport Mechanisms for Inducing Dynamic Nuclear Polarization in Magnetic Resonance Microsystems: Dynamical Theory, Design Rules, and Experimental Protocols, Black Forest Focus on Soft Matter 6 “Magnetic Resonance Microsystems”; Saig/Titisee, Black Forest, Germany, 2011.

13. J. A. Marohn, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, and J. H. Freed, Force-gradient detection of electron spin resonance from a nitroxide spin label: A path to single-nitroxide sensitivity and applications in biology, National Biomedical Center for Advanced Electron Spin Resonance Technology (ACERT) Workshop on Electron Spin Resonance Microscopy; Ithaca, New York; January 16 – 18, 2011, [url].

14. A. O. Hero, Sparsity constrained image reconstructions, Air Force Research Laboratory Workshop on Tomography in Materials Science (Jeff Simmons, organizer); Dayton, Ohio; December, 2010.

15. J. G. Longenecker, Fabrication of Integrated Nanomagnets Overhanging Batch- Fabricated Attonewton-Sensitivity Cantilevers, Cornell NanoScale Facility Annual Meeting; Ithaca, New York; September 16, 2010, [url].

16. J. A. Marohn, Force-Gradient Detection of Electron Spin Resonance from a Nitroxide Spin Label: A Path to Applications, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, 2010, [url].

17. J. A. Marohn, Magnetic Resonance Force Microscopy Tutorial, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, 2010, [url].

18. J. A. Marohn, Advances in Nanoscale Magnetic Resonance Imaging, Michigan State University, Department of Physics; East Lansing, Michigan; March 1, 2010.

19. J. A. Marohn, Advances in Nanoscale Magnetic Resonance Imaging: Force-gradient detection of electron spin resonance from a nitroxide spin label and New physical effectsfor coupling spin magnetization to a mechanical oscillators, University of Texas at Austin, Department of Physics; Austin, Texas; November 17, 2009.

20. J. A. Marohn, What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance, Yale University; Department of Chemistry and Department of Physics (joint seminar); New Haven, Connecticut; November 3, 2009.

21. J. A. Marohn, What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance, Columbia University, Energy Frontier Research Center; New York, New York; October 29, 2009.

22. J. A. Marohn, A Road Map for Structural Characterization of Individual Biomacromolecules and Macromolecular Complexes via Detection and Imaging of Electron Spin Resonance from Single Nitroxide Spin Probes, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, 2009, [url].

23. J. A. Sidles, J. L. Garbini, J. P. Jacky, R. Picone, and S. Harsila, Tutorial: Practical recipes for the simulation of large-scale open quantum systems, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, 2009, [url].

24. A. O. Hero, Sparsity Constrained Image Reconstruction for MRFM, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, 2009, [url].

Number of Presentations: 24.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

John Sidles was awarded The G¨ unther Laukien Prize, among the highest honors awarded to researchers in the field of magnetic resonance. He shared the prize with Daniel Rugar and H. Jonathan Mamin, both of the IBM Almaden Research Center in San Jose, California, for their conception, implementation and application of Magnetic Resonance Force Microscopy. The award was presented at the 52nd annual Experimental Nuclear Magnetic Resonance Conference; Pacific Grove, California; April 10 – 15, 2011.

– A. O. Hero was awarded a University of Michigan Distinguished Faculty Achievement Award in 2011.

– Nikolas Hoepker was selected to take part in the 62nd Lindau Nobel Laureate Meeting (dedicated to Physics); Lindau, Germany; July 1 – 6, 2012, [url].

- Jonilyn G. Longenecker, Best Paper Award, MEMS and NEMS Division, American Vacuum Society 58th International Symposium; Nashville, Tennesee; November, 2011.

– Jonilyn G. Longenecker was given the Nellie Yeh-Poh Lin Whetten Memorial Award, awarded by the Cornell Nanoscale Facility (CNF) to an "outstanding female graduate student working at the CNF who displays the highest level of enthusiasm and commitment to professionalism"; September, 2011, [url].

– Jonilyn G. Longenecker was one of 13 graduate students chosen by the U.S. National Nanotechnology Infrastructure Network (NNIN) to represent the United States at the two-week-long International Winter School for Graduate Students on the Science and Technology of Nanofabrication held in Bangalore, India; January, 2011, [url].

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Jonilyn G. Longenecker	0.50	
Se Un Park	0.50	
Hamed Firouzi	0.50	
Dae-Yon Jung	0.50	
Yilun Chen	0.50	
Rico Picone	0.50	
FTE Equivalent:	**3.00**	
Total Number:	**6**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Roni Mittleman	0.50
AmiWiesel	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
John Sidles	0.50	No
John Marohn	0.50	No
Al Hero	0.20	No
Joe Garbini	0.20	No
Lee Harrel	0.05	No
FTE Equivalent:	**1.45**	
Total Number:	**5**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Jia Ji	0.50	Computer and Computational Science and Electrical Enginee
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 1.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 1.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 1.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 1.00

Names of Personnel receiving masters degrees

NAME	
Rico Picone	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
S. A. Hickman	
M. Ting	
Total Number:	**2**

Names of other research staff

NAME	PERCENT_SUPPORTED
Jon Jacky	0.50
Doug Mounce	0.50
FTE Equivalent:	**1.00**
Total Number:	**2**

Sub Contractors (DD882)

1 a. Cornell University

1 b. Office of Sponsored Programs
373 Pine Tree Road
Ithaca NY 148502820

Sub Contractor Numbers (c):
Patent Clause Number (d-1):
Patent Date (d-2):
Work Description (e):
Sub Contract Award Date (f-1):
Sub Contract Est Completion Date(f-2):

---

1 a. Cornell University

1 b. Office of Sponsored Programs
373 Pine Tree Road
Ithaca NY 148502820

Sub Contractor Numbers (c):
Patent Clause Number (d-1):
Patent Date (d-2):
Work Description (e):
Sub Contract Award Date (f-1):
Sub Contract Est Completion Date(f-2):

---

1 a. University of Michigan - Ann Arbor

1 b. Office of Sponsored Programs
1058 Wolverine Tower
Ann Arbor MI 481091340

Sub Contractor Numbers (c):
Patent Clause Number (d-1):
Patent Date (d-2):
Work Description (e):
Sub Contract Award Date (f-1):
Sub Contract Est Completion Date(f-2):

---

1 a. University of Michigan - Ann Arbor

1 b. Regents of the University of Michigan
3003 S. State St
Ann Arbor MI 481091274

Sub Contractor Numbers (c):
Patent Clause Number (d-1):
Patent Date (d-2):
Work Description (e):
Sub Contract Award Date (f-1):
Sub Contract Est Completion Date(f-2):

Inventions (DD882)

Scientific Progress

The goal of this MURI was to detect magnetic resonance from an individual proton using magnetic resonance force microscopy (MRFM). Pushing MRFM to single-proton sensitivity requires meeting three experimental challenges:

1. Fabricating nanomagnets which produce a large magnetic field gradient and yet have only a thin damage layer. An MRFM experiment may be performed in either a ”sampleon- cantilever” configuration, with the sample affixed to the cantilever and brought near an independently fabricated nanomagnet, or in a ”magnet-on-cantilever” configuration, with the nanomagnet affixed to the cantilever and brought near a thinfilm sample. To allow for imaging the widest range of samples — including semiconductor devices and flash-frozen biological samples — we focused attention on preparing nanomagnets affixed to the leading edges of attonewton-sensitivity cantilevers [1; 2].

2. Understanding and mitigating the large non-contact friction (and frequency noise) typically experienced by an attonewton-sensitivity cantilever near a surface. In the highestsensitivity magnetic resonance force microscope experiments carried out to date, the cantilever force sensitivity has been limited not by intrinsic dissipation in the cantilever, but by spurious force (and frequency) fluctuations experienced by the cantilever near a surface. We have developed a first-principles understanding of this surface noise [3–8] in order to minimize it through improved cantilever design [1; 2] and sample preparation.

3. Devising a suitable spin detection protocol. The signals in an MRFM experiment are small. A central challenge in MRFM is devising spin-detection protocols which (1) perform well in the presence of surface noise and (2) are immune from artifacts caused by the microwave or radiowave perturbations applied to manipulate spin magnetization. The “i-OSCAR” spin-detection protocol invented by Dan Rugar and co-workers to detect single-electron magnetic resonance via MRFM met these exacting demands [9], but required samples with extraordinarily-long spin relaxation times to achieve single spin sensitivity. To extend single-electron spin detection to scientifically and technologically interesting samples clearly requires new spin-detection protocols [10; 11]. For single-proton spin detection, we have tried to determine whether force detection or force-gradient detection is more likely to succeed in generating a distinguishable signal.

Pushing MRFM to single-proton sensitivity also requires meeting a number of theoretical challenges: Devising image-reconstruction algorithms that work in the single-spin limit, when the signal-to- noise ratio is low and when the experimental knowledge of the shape and magnetization of the magnetic tip is uncertain. 2. Inventing an approach for simulating large numbers of spins, so that we may obtain a first-principles understanding of spin diffusion and dynamic nuclear polarization in the presence of the large magnetic field gradients present in an MRFM experiment.

Technology Transfer

ARO MURI Final Report

Principle Investigator
John A. SIDLES

Co-Principle Investigator
John A. MAROHN

Project Period
09/30/2011

Reporting Period
08/01/2009 – 09/30/2011

Grant Number
ARO W911NF-05-1-0403

Report Due Date
12/01/2011

Date
October 14, 2012

Contents

List of Figures

This MURI award, U.S. Army Research Office MURI grant W911NF-05-1-0403, was funded from 03/01/05 to 09/30/10; it was continued to 09/30/11 under a no-cost extension. This report summarizes progress during the entire funding period, with an emphasis on work accomplished during the final reporting period of the MURI — from 08/01/2009 to 09/30/2011.

1 People supported

- Graduate Students: 5
  - Ms. Jonilyn G. Longenecker (JGL)
    Department of Chemistry and Chemical Biology; Cornell University; Ithaca, New York
    Support: ARO MURI funds provided salary support and supplies during AY 2009 – 2010. ARO MURI funds were used to pay for laboratory supplies and expendables through 2010/09. From 2010/05 to 2012/05 JGL's salary support was provided by the NSF through grants EEC-0117770 and EEC-0646547 to the Cornell Center for Nanoscale Systems.
  - Se Un Park
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
  - Hamed Firouzi
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
  - Dae-Yon Jung
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
  - Yilun Chen
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
- Faculty: 4
  - Prof. John A. Sidles
    Department of Orthopaedics and Sports Medicine; University of Washington; Seattle, Washington.
  - Prof. Albert O. Hero
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
  - Prof. John A. Marohn
    Department of Chemistry and Chemical Biology; Cornell University; Ithaca, New York.

Support: ARO MURI funds provided summer salary 2011/05/16 – 2011/05/31 (0.5 month), summer salary 2010/06/16 – 2010/06/30 (0.5 month), and paid for supplies through 2010/09.

– Prof. Lee E. Harrell
Department of Physics and Nuclear Engineering; U.S. Military Academy; West Point, New York.
Support: ARO MURI funds provided supplies in 2010/06 and 2011/06 during collaborative work carried out in Marohn's laboratory at Cornell University.

- Postdocs: 2
  - Roni Mittleman, Ph.D.
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
    Presently a postdoc at the University of Michigan.
  - Ami Wiesel, Ph.D.
    Department of Electrical Engineering and Computer Science; University of Michigan; Ann Arbor, Michigan.
    Presently an Assistant Professor at Hebrew University.
- Undergraduates: 1
  - Jia Ji. This senior University of Michigan undergraduate student worked on sparse reconstruction in Winter 2011. She is now first year graduate student at Stanford University.
- Undergrad Metrics:
  - number funded and graduated: 1
  - number funded and graduated and in STEM: 0
  - number funded and graduated to graduate MS or PhD: 1
  - number funded and graduated to work at DoD: 0
  - number funded and graduated with 3.5 GPA: 1
  - number funded and graduated by a DoD Ctr. of Excellence: 0
  - number funded and graduated who received STEM scholarships: 0
- Other Research Staff: 0
- PhD's awarded: 2
  - S. A. Hickman *Batch fabrication of cantilevered magnetic nanorods on attonewton-sensitivity silicon oscillators for magnetic resonance force microscopy* PhD thesis, Cornell University, Ithaca, New York, **2010**, [url]. Thesis filed February, 2010.
    Support: ARO MURI funds provided salary support during AY 2008 – 2009.

– M. Ting *Signal processing for magnetic resonance force microscopy* PhD thesis, University of Michigan, Ann Arbor, **2006**.

- Master's awarded: 0

2 Output

2.1 Papers

- Number of peer review papers submitted or in preparation: 3

1. L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, Long-lived frequency shifts observed in a magnetic resonance force microscope experiment following microwave irradiation of a nitroxide spin probe, *Appl. Phys. Lett.*, **2012**, *in preparation*.
2. E. W. Moore, S.-G. Lee, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, The in-plane to out-of-plane switching of a single-domain magnet affixed to a cantilevered beam, *Phys. Rev. B*, **2012**, *in preparation*.
3. S.-U. Park, N. Dobigeon, and A. O. Hero, Variational semi-blind sparse deconvolutionwith orthogonal kernel bases, *IEEE Trans. on Image Process.*, **2011**, *submitted*.

- Number of peer review papers in print or in press: 10

1. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient nanomagnets on cantilevers for sensitive detection of nuclear magnetic resonance, *ACS Nano*, **2012**, *in press*, [url].
2. S. U. Park, N. Dobigeon, and A. O. Hero, Semi-blind sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2012**, *21*, 3838 – 3849, [url].
3. D. A. Alexson, S. A. Hickman, J. A. Marohn, and D. D. Smith, Single-shot nuclear magnetization recovery curves with force-gradient detection, *Appl. Phys. Lett.*, **2012**, *101*, 022103, [url].
4. S.-G. Lee, E. W. Moore, and J. A. Marohn, A unified picture of cantilever frequency-shift measurements of magnetic resonance, *Phys. Rev. B*, **2012**, *85*, 165447, [url].
5. S.-G. Lee, E. W. Moore, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, Switching through intermediate states seen in a single nickel nanowire by cantilever magnetometry, *J. Appl. Phys.*, **2012**, *111*, 083911, [url].
6. J. G. Longenecker, E. W. Moore, and J. A. Marohn, Rapid serial prototyping of magnet-tipped attonewton-sensitivity cantilevers by focused ion beam manipulation, *J. Vac. Sci. Technol. B*, **2011**, *29*, 032001, [url].

7. S. A. Hickman, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. J. Wright, L. E. Harrell, and J. A. Marohn, Batch-fabrication of cantilevered magnets on attonewton-sensitivity mechanical oscillators for scanned-probe nanoscale magnetic resonance imaging, *ACS Nano*, **2010**, *4*, 7141 – 7150, [url].
8. E. W. Moore, S.-G. Lee, S. A. Hickman, L. E. Harrell, and J. A. Marohn, Evading surface- and detector frequency noise in harmonic oscillator measurements of force gradients, *Appl. Phys. Lett.*, **2010**, *97*, 044105, [url].
9. E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, J. H. Freed, and J. A. Marohn, Scanned-probe detection of electron spin resonance from a nitroxide spin probe, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 22251 – 22256, [url].
10. N. Dobigeon, A. Hero, and J.-Y. Tourneret, Hierarchical bayesian sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2009**, *18*, 2059 – 2070, [url].

- Number of Non Peer Reviewed Papers: 0
- Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

1. S.-U. Park, N. Dobigeon, and A. O. Hero Myopic reconstruction and its application to MRFM. In *SPIE Electronic Imaging Conference; San Jose, California; January 23 – 27*, 2011, [url].

- Number of Non-Peer-Reviewed Conference Proceeding publications (other than abstracts): 0
- Number of Books: 0

2.2 Presentations, honors, and awards

- Honors and Awards: 6
  - John Sidles was awarded The Günther Laukien Prize, among the highest honors awarded to researchers in the field of magnetic resonance. He shared the prize with Daniel Rugar and H. Jonathan Mamin, both of the IBM Almaden Research Center in San Jose, California, for their conception, implementation and application of Magnetic Resonance Force Microscopy. The award was presented at the 52nd annual Experimental Nuclear Magnetic Resonance Conference; Pacific Grove, California; April 10 – 15, 2011.
  - A. O. Hero was awarded a University of Michigan Distinguished Faculty Achievement Award in 2011.
  - Nikolas Hoepker was selected to take part in the 62nd Lindau Nobel Laureate Meeting (dedicated to Physics); Lindau, Germany; July 1 – 6, **2012**, [url].

- Jonilyn G. Longenecker, Best Paper Award, MEMS and NEMS Division, American Vacuum Society 58th International Symposium; Nashville, Tennesee; November, **2011**.
- Jonilyn G. Longenecker was given the Nellie Yeh-Poh Lin Whetten Memorial Award, awarded by the Cornell Nanoscale Facility (CNF) to an "outstanding female graduate student working at the CNF who displays the highest level of enthusiasm and commitment to professionalism"; September, **2011**, [url].
- Jonilyn G. Longenecker was one of 13 graduate students chosen by the U.S. National Nanotechnology Infrastructure Network (NNIN) to represent the United States at the two-week-long International Winter School for Graduate Students on the Science and Technology of Nanofabrication held in Bangalore, India; January, **2011**, [url].

• Number of Oral Presentations (Invited): 24

1. J. A. Marohn, *Using Cantilevers to Probe Carrier Diffusion and the Electronic Energy Levels of Charged Defects in Films of Organic Semiconductors*, Materials Research Society Fall Meeting; Boston, Massachusetts; November 26 – 30, **2012**, [url].
2. J. A. Marohn, *Charting a path to 1 nm resolution magnetic resonance imaging of biomacromolecules: High-gradient magnet-tipped cantilevers and dynamic nuclear polarization in magnetic resonance force microscopy*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].
3. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *Development and characterization of high-gradient cobalt-tipped cantilevers*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].
4. R. Picone, J. Garbini, and J. A. Sidles, *Separatory Magnetic Transport in Magnetic Resonance Force Microscopy*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].
5. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *High gradient cobalt nanomagnets integrated on attonewton-sensitivity cantilevers for scanned probe magnetic resonance detection of nuclear spins*, Gordon Research Conference on Nanostructure Fabrication; Biddeford, Maine; July 15 – 20, **2012**, [url].
6. J. A. Marohn, *Using cantilevers to detect magnetic resonance, spectroscopically probe electronic energy levels, and image charge generation at the nanoscale*, Cornell Center for Materials Research Symposium, Next-Generation Materials Characterization; Ithaca, New York; May 22, **2012**, [url].
7. J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. Rettner, D. Rugar, and J. A. Marohn, *Nanofabrication of magnet-tipped, high gradient cantilevers for scanned probe nano-MRI*, First Quadrennial Juniata College Chemistry Alumni Symposium; Huntingdon, Pennsylvania; April 13 – 14, **2012**.

8. J. A. Marohn, *Towards Nanometer Resolution Single Particle Imaging by Mechanically Detected Magnetic Resonance*, The Scripps Research Institute; La Jolla, California; January 4, **2012**.

9. J. A. Marohn, *Discussion Leader, Electron and Nuclear Spins (Part 1)*, Gordon Research Conference on Magnetic Resonance; Biddeford, Maine; June 12 – 17, **2011**, [url].

10. J. G. Longenecker, *Electron spin resonance detection of nitroxide labels by magnetic resonance force microscopy*, Gordon Research Seminar on Magnetic Resonance; Biddeford, Maine; June 11 – 12, **2011**.

11. J. A. Marohn, *Mechanically Detected Magnetic Resonance from TEMPAMINE and the Feasibility of Imaging Single-Spin EPR from such a Workhorse Spin Probe*, Session on Frontiers of Electron Paramagnetic Resonance in Biological and Inorganic Materials; Eastern Analytical Symposium; Somerset, New Jersey; November 14 – 17, **2011**.

12. J. A. Sidles, *Transport Mechanisms for Inducing Dynamic Nuclear Polarization in Magnetic Resonance Microsystems: Dynamical Theory, Design Rules, and Experimental Protocols*, Black Forest Focus on Soft Matter 6 "Magnetic Resonance Microsystems"; Saig/Titisee, Black Forest, Germany, **2011**.

13. J. A. Marohn, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, and J. H. Freed, *Force-gradient detection of electron spin resonance from a nitroxide spin label: A path to single-nitroxide sensitivity and applications in biology*, National Biomedical Center for Advanced Electron Spin Resonance Technology (ACERT) Workshop on Electron Spin Resonance Microscopy; Ithaca, New York; January 16 – 18, **2011**, [url].

14. A. O. Hero, *Sparsity constrained image reconstructions*, Air Force Research Laboratory Workshop on Tomography in Materials Science (Jeff Simmons, organizer); Dayton, Ohio; December, **2010**.

15. J. G. Longenecker, *Fabrication of Integrated Nanomagnets Overhanging Batch-Fabricated Attonewton-Sensitivity Cantilevers*, Cornell NanoScale Facility Annual Meeting; Ithaca, New York; September 16, **2010**, [url].

16. J. A. Marohn, *Force-Gradient Detection of Electron Spin Resonance from a Nitroxide Spin Label: A Path to Applications*, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, **2010**, [url].

17. J. A. Marohn, *Magnetic Resonance Force Microscopy Tutorial*, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, **2010**, [url].

18. J. A. Marohn, *Advances in Nanoscale Magnetic Resonance Imaging*, Michigan State University, Department of Physics; East Lansing, Michigan; March 1, **2010**.

19. J. A. Marohn, *Advances in Nanoscale Magnetic Resonance Imaging: Force-gradient detection of electron spin resonance from a nitroxide spin label and New physical effects*

for coupling spin magnetization to a mechanical oscillators, University of Texas at Austin, Department of Physics; Austin, Texas; November 17, **2009**.

20. J. A. Marohn, *What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance*, Yale University; Department of Chemistry and Department of Physics (joint seminar); New Haven, Connecticut; November 3, **2009**.
21. J. A. Marohn, *What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance*, Columbia University, Energy Frontier Research Center; New York, New York; October 29, **2009**.
22. J. A. Marohn, *A Road Map for Structural Characterization of Individual Biomacromolecules and Macromolecular Complexes via Detection and Imaging of Electron Spin Resonance from Single Nitroxide Spin Probes*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].
23. J. A. Sidles, J. L. Garbini, J. P. Jacky, R. Picone, and S. Harsila, *Tutorial: Practical recipes for the simulation of large-scale open quantum systems*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].
24. A. O. Hero, *Sparsity Constrained Image Reconstruction for MRFM*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

- Number of Oral Presentations (Contributed): 11

1. L. Chen, E. W. Moore, J. G. Longenecker, and J. A. Marohn, *ESR induced anomalous polarization in Magnetic Resonance Force Microscopy*, American Physical Society March Meeting; Boston, Massachusetts; February 27 – March 2, **2012**, [url].
2. J. G. Longenecker, E. W. Moore, and J. A. Marohn, *Rapid Serial Prototyping of Magnet-Tipped Attonewton-Sensitivity Cantilevers*, American Vacuum Society 58th International Symposium and Exhibition; Nashville, Tennessee; October 30 – November 4, **2011**, [url].
3. L. Harrell, E. Moore, S. Lee, S. Hickman, and J. Marohn, *Parametric Amplification Protocol for Frequency-Modulated Magnetic Resonance Force Microscopy Signals*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].
4. J. A. Marohn, E. Moore, and J. Longenecker, *Rapid Serial Prototyping and Analysis of Nanomagnet-Tipped Attonewton-Sensitivity Cantilevers for Magnetic Resonance Force Microscopy*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].

5. E. W. Moore, S. Lee, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, *Cantilever torque magnetometry studies of the in-plane to out-of-plane transition in a single nickel magnetic nanorod*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].

6. J. G. Longenecker, S. A. Hickman, E. W. Moore, S.-G. Lee, S. J. Wright, L. E. Harrell, and J. A. Marohn, *Fabrication of Integrated Nanomagnets Overhanging Batch-Fabricated Attonewton-Sensitivity Cantilevers*, 57th International Symposium and Exhibition; Albuquerque, New Mexico; October 17 – 22, **2010**, [url].

7. E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. W. andLee E. Harrell, J. G. Longenecker, P. P. Borbat, J. H. Freed, and J. A. Marohn, *High sensitivity electron spin magnetic resonance force microscopy for labeled biological samples*, American Physical Society March Meeting; Portland, Oregon; March 15 – 19, **2010**, [url].

8. S.-G. Lee, E. W. Moore, S. A. Hickman, L. E. Harrell, and J. A. Marohn, *Non-degenerate parametric amplification used for surface noise evasion in scanned probe microscopy*, American Physical Society March Meeting; Portland, Oregon; March 15 – 19, **2010**, [url].

9. J. G. Longenecker, S. Hickman, L. Harrell, and J. Marohn, *Fabrication of overhanging magnet-tipped cantilevers for nanoscale scanned-probe magnetic resonance*, American Vacuum Society 56th International Symposium and Exhibition; San Jose, California; November 8 – 13, **2009**, [url].

10. S.-G. Lee, *New Physics for Coupling Spin Magnetization to a Mechanical Oscillator*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

11. S. A. Hickman, *Batch Fabrication of Overhanging sub-100 nm Diameter Nickel Nanorods on Attonewton Sensitivity Silicon Cantilevers*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

2.3 Intellectual property

- Number of Patents Disclosed: 0
- Number of Patents Awarded: 0

2.4 Technology transfer

Any specific interactions or developments which would constitute technology transfer of the research results. Examples include interaction with other DOD scientists, interactions with industry, initiation of a start- up company based on research results or transfer of information which might impact the development of products.

- **SC Solutions**. The Cornell team, in collaboration with Dr. Doran Smith of the U.S. Army Research Laboratory, previously worked together in an ARO-funded Phase II Small Business Technology Transfer Research Grant with SC Solutions (Sunnyvale, CA) and CryoIndustries of America (Manchester, NH). This collaboration previously resulted in two joint publications [52; 53]. During the reporting period, SC Solutions delivered an FPGA-based cantilever controller to the marketplace. Product details can be found at http://www.scsolutions.com/public/product/mrfm-controllers.html.

- **IBM**. The Hero-team's interactions with Dan Rugar and coworkers led to acknowledgements of these contributions in his recent paper [54]. Graduate student Jonilyn Longenecker and postdoc Lei Chen of Cornell University spent a week at IBM Almaden Research Center to execute a joint research project with Dr. John Mamin and Dr. Dan Rugar (Almaden, California; November 10 – 18, 2011). They had previously visited, along with Marohn, the laboratory of Daniel Rugar at IBM Almaden to learn advanced experimental techniques in magnetic resonance force microscopy (Almaden, California; October 12 – 13, 2009). The Cornell/IBM collaboration will result in one joint publication [6].

- **USMA**. Marohn's team at Cornell hosted and carried out joint research with Prof. Lee Harrell of the U.S. Military Academy at West Point (June 2010 and June 2011). The Cornell/USMA collaboration resulted in three joint publications [12–14].

- **USARL**. Visited, along with two graduate students, the laboratory of Dr. Doran Smith at the U.S. Army Research Laboratory to learn advanced experimental techniques in magnetic resonance force microscopy (Adelphi, Maryland; April 24, 2010). Supplied attonewton-sensitivity cantilevers to Smith's team and interacted with him *via* email biweekly (approximately) during the reporting period. The Cornell/USARL collaboration resulted in one joint publication [8].

- **NIH**. Visited, along with two graduate students, the laboratory of Dr. Sriram Subramaniam at the National Institutes of Health to learn about cryo-electron microscopy and preparing biological samples for study in vacuum at cryogenic temperatures (Bethesda, Maryland; April 21, 2010).

- Interacted with Dr. Doran Smith (US ARL) and Drs. John Mamin and Dan Rugar (IBM Almaden) during Army Research Office Multi-University Research Institute (ARO/MURI) program review meetings.
  - Almaden, California; September 29 – 30, 2011.
  - Washington, DC; April 22 – 23, 2010.

2.5 Bibliography

[1] S. A. Hickman *Batch fabrication of cantilevered magnetic nanorods on attonewton-sensitivity silicon oscillators for magnetic resonance force microscopy* PhD thesis, Cornell University, Ithaca, New York, **2010**, [url].

[2] M. Ting *Signal processing for magnetic resonance force microscopy* PhD thesis, University of Michigan, Ann Arbor, **2006**.

[3] L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, Long-lived frequency shifts observed in a magnetic resonance force microscope experiment following microwave irradiation of a nitroxide spin probe, *Appl. Phys. Lett.*, **2012**, *in preparation*.

[4] E. W. Moore, S.-G. Lee, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, The in-plane to out-of-plane switching of a single-domain magnet affixed to a cantilevered beam, *Phys. Rev. B*, **2012**, *in preparation*.

[5] S.-U. Park, N. Dobigeon, and A. O. Hero, Variational semi-blind sparse deconvolutionwith orthogonal kernel bases, *IEEE Trans. on Image Process.*, **2011**, *submitted*.

[6] J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient nanomagnets on cantilevers for sensitive detection of nuclear magnetic resonance, *ACS Nano*, **2012**, *in press*, [url].

[7] S. U. Park, N. Dobigeon, and A. O. Hero, Semi-blind sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2012**, *21*, 3838 – 3849, [url].

[8] D. A. Alexson, S. A. Hickman, J. A. Marohn, and D. D. Smith, Single-shot nuclear magnetization recovery curves with force-gradient detection, *Appl. Phys. Lett.*, **2012**, *101*, 022103, [url].

[9] S.-G. Lee, E. W. Moore, and J. A. Marohn, A unified picture of cantilever frequency-shift measurements of magnetic resonance, *Phys. Rev. B*, **2012**, *85*, 165447, [url].

[10] S.-G. Lee, E. W. Moore, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, Switching through intermediate states seen in a single nickel nanowire by cantilever magnetometry, *J. Appl. Phys.*, **2012**, *111*, 083911, [url].

[11] J. G. Longenecker, E. W. Moore, and J. A. Marohn, Rapid serial prototyping of magnet-tipped attonewton-sensitivity cantilevers by focused ion beam manipulation, *J. Vac. Sci. Technol. B*, **2011**, *29*, 032001, [url].

[12] S. A. Hickman, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. J. Wright, L. E. Harrell, and J. A. Marohn, Batch-fabrication of cantilevered magnets on attonewton-sensitivity mechanical oscillators for scanned-probe nanoscale magnetic resonance imaging, *ACS Nano*, **2010**, *4*, 7141 – 7150, [url].

[13] E. W. Moore, S.-G. Lee, S. A. Hickman, L. E. Harrell, and J. A. Marohn, Evading surface- and detector frequency noise in harmonic oscillator measurements of force gradients, *Appl. Phys. Lett.*, **2010**, *97*, 044105, [url].

[14] E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, J. H. Freed, and J. A. Marohn, Scanned-probe detection of electron spin resonance from a nitroxide spin probe, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 22251 – 22256, [url].

[15] N. Dobigeon, A. Hero, and J.-Y. Tourneret, Hierarchical bayesian sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2009**, *18*, 2059 – 2070, [url].

[16] S.-U. Park, N. Dobigeon, and A. O. Hero Myopic reconstruction and its application to MRFM. In *SPIE Electronic Imaging Conference; San Jose, California; January 23 – 27*, 2011, [url].

[17] J. A. Marohn, *Using Cantilevers to Probe Carrier Diffusion and the Electronic Energy Levels of Charged Defects in Films of Organic Semiconductors*, Materials Research Society Fall Meeting; Boston, Massachusetts; November 26 – 30, **2012**, [url].

[18] J. A. Marohn, *Charting a path to 1 nm resolution magnetic resonance imaging of biomacromolecules: High-gradient magnet-tipped cantilevers and dynamic nuclear polarization in magnetic resonance force microscopy*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].

[19] J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *Development and characterization of high-gradient cobalt-tipped cantilevers*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].

[20] R. Picone, J. Garbini, and J. A. Sidles, *Separatory Magnetic Transport in Magnetic Resonance Force Microscopy*, NanoMRI Conference 2012; Ascona, Switzerland; July 22 – 27, **2012**, [url].

[21] J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, *High gradient cobalt nanomagnets integrated on attonewton-sensitivity cantilevers for scanned probe magnetic resonance detection of nuclear spins*, Gordon Research Conference on Nanostructure Fabrication; Biddeford, Maine; July 15 – 20, **2012**, [url].

[22] J. A. Marohn, *Using cantilevers to detect magnetic resonance, spectroscopically probe electronic energy levels, and image charge generation at the nanoscale*, Cornell Center for Materials Research Symposium, Next-Generation Materials Characterization; Ithaca, New York; May 22, **2012**, [url].

[23] J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. Rettner, D. Rugar, and J. A. Marohn, *Nanofabrication of magnet-tipped, high gradient cantilevers for scanned probe nano-MRI*, First Quadrennial Juniata College Chemistry Alumni Symposium; Huntingdon, Pennsylvania; April 13 – 14, **2012**.

[24] J. A. Marohn, *Towards Nanometer Resolution Single Particle Imaging by Mechanically Detected Magnetic Resonance*, The Scripps Research Institute; La Jolla, California; January 4, **2012**.

[25] J. A. Marohn, *Discussion Leader, Electron and Nuclear Spins (Part 1)*, Gordon Research Conference on Magnetic Resonance; Biddeford, Maine; June 12 – 17, **2011**, [url].

[26] J. G. Longenecker, *Electron spin resonance detection of nitroxide labels by magnetic resonance force microscopy*, Gordon Research Seminar on Magnetic Resonance; Biddeford, Maine; June 11 – 12, **2011**.

[27] J. A. Marohn, *Mechanically Detected Magnetic Resonance from TEMPAMINE and the Feasibility of Imaging Single-Spin EPR from such a Workhorse Spin Probe*, Session on Frontiers of Electron Paramagnetic Resonance in Biological and Inorganic Materials; Eastern Analytical Symposium; Somerset, New Jersey; November 14 – 17, **2011**.

[28] J. A. Sidles, *Transport Mechanisms for Inducing Dynamic Nuclear Polarization in Magnetic Resonance Microsystems: Dynamical Theory, Design Rules, and Experimental Protocols*, Black Forest Focus on Soft Matter 6 “Magnetic Resonance Microsystems”; Saig/Titisee, Black Forest, Germany, **2011**.

[29] J. A. Marohn, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, and J. H. Freed, *Force-gradient detection of electron spin resonance from a nitroxide spin label: A path to single-nitroxide sensitivity and applications in biology*, National Biomedical Center for Advanced Electron Spin Resonance Technology (ACERT) Workshop on Electron Spin Resonance Microscopy; Ithaca, New York; January 16 – 18, **2011**, [url].

[30] A. O. Hero, *Sparsity constrained image reconstructions*, Air Force Research Laboratory Workshop on Tomography in Materials Science (Jeff Simmons, organizer); Dayton, Ohio; December, **2010**.

[31] J. G. Longenecker, *Fabrication of Integrated Nanomagnets Overhanging Batch-Fabricated Attonewton-Sensitivity Cantilevers*, Cornell NanoScale Facility Annual Meeting; Ithaca, New York; September 16, **2010**, [url].

[32] J. A. Marohn, *Force-Gradient Detection of Electron Spin Resonance from a Nitroxide Spin Label: A Path to Applications*, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, **2010**, [url].

[33] J. A. Marohn, *Magnetic Resonance Force Microscopy Tutorial*, 3rd International Conference on Nano Magnetic Resonance Imaging; Le Tremblay-sur-Mauldre, France; July 12 – 16, **2010**, [url].

[34] J. A. Marohn, *Advances in Nanoscale Magnetic Resonance Imaging*, Michigan State University, Department of Physics; East Lansing, Michigan; March 1, **2010**.

[35] J. A. Marohn, *Advances in Nanoscale Magnetic Resonance Imaging: Force-gradient detection of electron spin resonance from a nitroxide spin label and New physical effects for coupling spin magnetization to a mechanical oscillators*, University of Texas at Austin, Department of Physics; Austin, Texas; November 17, **2009**.

[36] J. A. Marohn, *What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance*, Yale University; Department of Chemistry and Department of Physics (joint seminar); New Haven, Connecticut; November 3, **2009**.

[37] J. A. Marohn, *What's really going on down there? Insights into organic electronic materials and devices from electric force microscopy and Nanoscale magnetic resonance imaging via mechanically detected magnetic resonance*, Columbia University, Energy Frontier Research Center; New York, New York; October 29, **2009**.

[38] J. A. Marohn, *A Road Map for Structural Characterization of Individual Biomacromolecules and Macromolecular Complexes via Detection and Imaging of Electron Spin Resonance from Single Nitroxide Spin Probes*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[39] J. A. Sidles, J. L. Garbini, J. P. Jacky, R. Picone, and S. Harsila, *Tutorial: Practical recipes for the simulation of large-scale open quantum systems*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[40] A. O. Hero, *Sparsity Constrained Image Reconstruction for MRFM*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[41] L. Chen, E. W. Moore, J. G. Longenecker, and J. A. Marohn, *ESR induced anomalous polarization in Magnetic Resonance Force Microscopy*, American Physical Society March Meeting; Boston, Massachusetts; February 27 – March 2, **2012**, [url].

[42] J. G. Longenecker, E. W. Moore, and J. A. Marohn, *Rapid Serial Prototyping of Magnet-Tipped Attonewton-Sensitivity Cantilevers*, American Vacuum Society 58th International Symposium and Exhibition; Nashville, Tennessee; October 30 – November 4, **2011**, [url].

[43] L. Harrell, E. Moore, S. Lee, S. Hickman, and J. Marohn, *Parametric Amplification Protocol for Frequency-Modulated Magnetic Resonance Force Microscopy Signals*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].

[44] J. A. Marohn, E. Moore, and J. Longenecker, *Rapid Serial Prototyping and Analysis of Nanomagnet-Tipped Attonewton-Sensitivity Cantilevers for Magnetic Resonance Force Microscopy*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].

[45] E. W. Moore, S. Lee, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, *Cantilever torque magnetometry studies of the in-plane to out-of-plane transition in a single nickel magnetic nanorod*, American Physical Society March Meeting; Dallas, Texas; March 21 – 25, **2011**, [url].

[46] J. G. Longenecker, S. A. Hickman, E. W. Moore, S.-G. Lee, S. J. Wright, L. E. Harrell, and J. A. Marohn, *Fabrication of Integrated Nanomagnets Overhanging Batch-Fabricated Attonewton-Sensitivity Cantilevers*, 57th International Symposium and Exhibition; Albuquerque, New Mexico; October 17 – 22, **2010**, [url].

[47] E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. W. andLee E. Harrell, J. G. Longenecker, P. P. Borbat, J. H. Freed, and J. A. Marohn, *High sensitivity electron spin magnetic resonance force microscopy for labeled biological samples*, American Physical Society March Meeting; Portland, Oregon; March 15 – 19, **2010**, [url].

[48] S.-G. Lee, E. W. Moore, S. A. Hickman, L. E. Harrell, and J. A. Marohn, *Non-degenerate parametric amplification used for surface noise evasion in scanned probe microscopy*, American Physical Society March Meeting; Portland, Oregon; March 15 – 19, **2010**, [url].

[49] J. G. Longenecker, S. Hickman, L. Harrell, and J. Marohn, *Fabrication of overhanging magnet-tipped cantilevers for nanoscale scanned-probe magnetic resonance*, American Vacuum Society 56th International Symposium and Exhibition; San Jose, California; November 8 – 13, **2009**, [url].

[50] S.-G. Lee, *New Physics for Coupling Spin Magnetization to a Mechanical Oscillator*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[51] S. A. Hickman, *Batch Fabrication of Overhanging sub-100 nm Diameter Nickel Nanorods on Attonewton Sensitivity Silicon Cantilevers*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[52] D. de Roover, L. M. Porter II, A. Emami-Naeni, J. A. Marohn, S. Kuehn, S. Garner, and D. D. Smith , An all-digital cantilever controller for MRFM and scanned probe microscopy using a combined DSP/FPGA design. In *Proceedings of the 10th NSTI Nanotech Conference, Santa Clara, CA, U.S.A.*, 2007, [url].

[53] D. de Roover, L. M. Porter II, A. Emami-Naeni, J. A. Marohn, S. Kuehn, S. Garner, and D. D. Smith, An all-digital cantilever controller for MRFM and scanned probe microscopy using a combined DSP/FPGA design, *Amer. Laboratory*, **2008**, *40*, 12.

[54] C. L. Degen, M. Poggio, H. J. Mamin, C. T. Rettner, and D. Rugar, Nanoscale magnetic resonance imaging, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 1313 – 1317, [url].

3 Scientific progress and accomplishments

3.1 Introduction

The goal of this MURI was to detect magnetic resonance from an individual proton using magnetic resonance force microscopy (MRFM). Pushing MRFM to single-proton sensitivity requires meeting three experimental challenges:

1. *Fabricating nanomagnets which produce a large magnetic field gradient and yet have only a thin damage layer*. An MRFM experiment may be performed in either a "sample-on-cantilever" configuration, with the sample affixed to the cantilever and brought near an independently fabricated nanomagnet, or in a "magnet-on-cantilever" configuration, with the nanomagnet affixed to the cantilever and brought near a thin-film sample. To allow for imaging the widest range of samples — including semiconductor devices and flash-frozen biological samples — we focused attention on preparing nanomagnets affixed to the leading edges of attonewton-sensitivity cantilevers [1; 2].

2. *Understanding and mitigating the large non-contact friction (and frequency noise) typically experienced by an attonewton-sensitivity cantilever near a surface*. In the highest-sensitivity magnetic resonance force microscope experiments carried out to date, the cantilever force sensitivity has been limited not by intrinsic dissipation in the cantilever, but by spurious force (and frequency) fluctuations experienced by the cantilever near a surface. We have developed a first-principles understanding of this surface noise [3–8] in order to minimize it through improved cantilever design [1; 2] and sample preparation.

3. *Devising a suitable spin detection protocol*. The signals in an MRFM experiment are small. A central challenge in MRFM is devising spin-detection protocols which (1) perform well in the presence of surface noise and (2) are immune from artifacts caused by the microwave or radiowave perturbations applied to manipulate spin magnetization. The "i-OSCAR" spin-detection protocol invented by Dan Rugar and co-workers to detect single-electron magnetic resonance *via* MRFM met these exacting demands [9], but required samples with extraordinarily-long spin relaxation times to achieve single spin sensitivity. To extend single-electron spin detection to scientifically and technologically interesting samples clearly requires new spin-detection protocols [10; 11]. For single-proton spin detection, we have tried to determine whether force detection or force-gradient detection is more likely to succeed in generating a distinguishable signal.

Pushing MRFM to single-proton sensitivity also requires meeting a number of theoretical challenges:

1. *Devising image-reconstruction algorithms* that work in the single-spin limit, when the

signal-to- noise ratio is low and when the experimental knowledge of the shape and magnetization of the magnetic tip is uncertain.

2. *Inventing an approach for simulating large numbers of spins*, so that we may obtain a first-principles understanding of spin diffusion and dynamic nuclear polarization in the presence of the large magnetic field gradients present in an MRFM experiment.

3.2 Accomplishments

This MURI's funding began on 2005/03/01, ended on 2010/09/30, and was continued under a no-cost extension until 2011/09/30. Here we summarize progress made during the entire project, highlighting progress made during the final reporting period from 2009/08/01 to 2011/09/30.

3.2.1 Fabricating nanomagnets on attonewton-sensitivity cantilevers

Addressing this challenge was the Marohn team's main contribution to the MURI effort.

Spin sensitivity in a magnetic resonance force microscope measurement is proportional to the cantilever's force sensitivity and inversely proportional to the available magnetic field gradient. Achieving a large magnetic field gradient requires fabricating magnets with a small diameter and bringing the sample as close as possible to the magnet. It is thus essential that the cantilever maintain its force sensitivity at small cantilever-sample separations (in magnet-on-cantilever experiments) or at small cantilever-magnet separations (in sample-on-cantilever experiments).

3.2.1.1 Radio frequency cantilevers

In the first half of the MURI, the Marohn team developed both audiofrequency and radiofrequency cantilevers for MRFM. Audio frequency cantilevers had exhibited attonewton sensitivity [12; 13] provided they were made sufficiently thin, narrow, and long, and were cooled to temperatures of 4.2 kelvin or below. Radio frequency cantilevers had also been developed [14; 15], but at the time the MURI began the force sensitivity of rf cantilevers was inferior to the force sensitivity of audio frequency cantilevers [16].

Reasoning as follows, we nevertheless expected rf cantilevers to better maintain their force sensitivity at small tip-sample separations. According to the fluctuation-dissipation theorem, the force sensitivity of a cantilever is proportional to temperature and the dissipation (e.g., damping) experienced by the cantilever. A major source of cantilever damping near a surface arises from charges on the cantilever interacting with surface electric field fluctuations in the sample [17], with the cantilever dissipation proportional to the spectral density of electric field fluctuations at the cantilever resonance frequency. Over polymeric samples these fluctuating electric fields arise from thermal dielectric fluctuations [3; 4]. The dielectric response of most polymers, including biopolymers, falls off at frequencies above a few hundred kHz. One would therefore expect a cantilever with a resonance frequency in the MHz range to exhibit much less dissipation near a polymer surface than a cantilever with a resonance frequency in the kHz range.

When we began the MURI, there were many examples of radiofrequency cantilevers, but the great majority were doubly-clamped beams and therefore unsuitable for scanned probe experiments. A second challenge, when we began, was devising a scheme for detecting the motion of the rf cantilever. Laser interferometry has been used, but did not have the sensitivity to detect the thermal Brownian motion in the (high spring constant) rf cantilever. The most commonly used detection scheme was magnetomotive detection. This method required the cantilever beam to be attached at each end to a substrate and was therefore unsuitable for scanned probe experiments.

In previous reports we described in detail our (unpublished) work developing silicon rf cantilevers by top-down nanofabrication for MRFM experiments, which we briefly summarize here. We began by fabricating doubly clamped beams and observing their motion *via* magneto-motive detection, demonstrating that operating at higher applied magnetic field for increased sensitivity also led to more readout-induced damping due to current fluctuations in the beam interacting with the applied magnetic field. In parallel, we invented and developed a method for fabricating an rf cantilever with an integrated tunnel sensor for reading out cantilever motion; we succeeded in making tunnel sensors by opening up a gap in a metal-film constriction using electromigration, although not on a tunnel sensor integrated with a cantilever. Finally, we succeeded in fabricating singly-clamped cantilevers with integrated (but untested) capacitance sensors; these cantilevers were free-standing and in principle suitable for scanned probe experiments.

At the end of Phase I of our MURI, we made the difficult decision to abandon our team's rf cantilever work due to budget constraints.

3.2.1.2 Audio frequency cantilevers

When we began the MURI, both ESR and NMR had been detected in a magnet-on-cantilever MRFM experiment. The magnetic tips in these experiments were prepared by affixing a few-micron diameter magnetic particle to the cantilever's leading edge by hand, with further focused ion beam milling used to prepare submicron tips.

Our team had previously demonstrated patterning of 100 nm scale nickel magnets on attonewton sensitivity cantilevers [18], but the yield was low and alignment challenges left us unable at that time to prepare tips close enough to the cantilever's leading edge for an MRFM experiment. Sean Garner in Marohn's group invented and demonstrated the idea of using anisotropic wet etching of silicon to prepare magnets overhanging a silicon edge. Garner demonstrated the process with nickel magnets defined using optical lithography and this work was extended by Marohn to magnets defined by e-beam lithography. Unfortunately, the process required silicon-on-insulator wafers with a $\langle 111 \rangle$-oriented silicon device layer; these became impossible to obtain in 2005, and the process could not be used to make magnetic-tipped cantilevers.

With MURI funding, Hickman at Cornell was able to attack the challenge of producing nanomagnetic tips overhanging the leading edge of a cantilever. This work was summarized in detail in previous reports. The key innovation was identifying and optimizing a dry isotropic silicon etch that did not etch nickel or cobalt. It should be appreciated that harnessing this innovation to produce MRFM cantilevers required a tremendous amount of process engineering and integration — the final cantilever fabrication sequence required carrying out over 40 processing steps, mastering 18 nanofabrication instruments, and required approximately three weeks of full-time effort in the Cornell NanoScale Science and Technology Facility. This reporting period we published the results of Hickman's work in his PhD thesis [19] and in a long paper in *ACS Nano* [1]. In Ref. 1 we demonstrated using one of Hickman's nickel-tipped cantilevers to detect electron spin resonance. Moreover, these cantilevers exhibited a record low surface-induced dissipation (for an audio frequency cantilever) at small tip-sample separations.

These findings established that (1) e-beam defined nanomagnet tips could be fabricated *en batch* overhanging the leading edges of attonewton-sensitivity cantilevers and (2) these nanomagnet-tipped cantilevers could be used to detect MRFM. The yield was extremely low, however. Furthermore, the agreement between the observed and the predicted field-dependence of the ESR-MRFM signal was poor, indicating that the tip was incompletely and non-uniformly magnetized. A subsequent student on Marohn's team, Jonilyn Longenecker, investigated the cause of the low yield. The primary problem was that the BOSCH etch used to remove the handle-wafer silicon beneath the cantilever involved high temperatures which promoted chemical reactions between the nickel or cobalt of the magnetic tip and the silicon in the underlying wafer. This finding, and our team's studies of barrier layers, were likewise detailed in prior reports.

During this reporting period, Longenecker developed a method for fabricating e-beam defined nickel and cobalt tips overhanging the leading edges of attonewton-sensitivity cantilevers. Her insight was to decouple the magnet fabrication from the cantilever fabrication to avoid exposing the magnets to high-temperature processing. To achieve this decoupling, magnets are prepared *via* e-beam lithography, evaporation, and liftoff on separate micron-scale "chips". These magnet-tipped chips are released, one at a time, from their supporting substrate using focused ion beam milling and attached to a cantilever *via* focused ion beam deposition. Although the chips are affixed to the cantilevers serially, the attachment process takes only a few hours and has excellent yield. Both the magnets and the cantilevers can be prepared beforehand *via* batch fabrication in high yield. A paper describing this approach to fabricating nickel nanomagnet tips was published during this reporting period in *Journal of Vacuum Science and Technology B* [20].

This semi-serial approach to producing magnet-tipped cantilevers greatly facilitates the optimization of magnet dimensions and the analysis of identically-processed magnetic material by X-ray photoelectron spectroscopy (XPS) and SQUID magnetometry. It also facilitates the analysis of individual magnets by high-resolution electron microscopy and electron spectroscopy. The ability to analyze nanomagnets and magnetic films in chemical detail at nanometer spatial resolution is an essential step in producing magnets for single-proton experiments, where less than 5 nm of damage at the magnet's leading edge is required.

In Ref. 20 the magnetic properties of an individual cobalt nanomagnet on a cantilever were assessed using frequency-shift cantilever magnetometry [21–23]. To successfully fabricate cobalt nanomagnets, the process of Ref. 20 was modified to eliminate high-temperature processing steps. In 2011/11, these tips were used to detect proton magnetic resonance in collaboration with Dan Rugar and John Mamin of the IBM Almaden Research Center. Tips were prepared at Cornell, flown to San Jose by Lone-

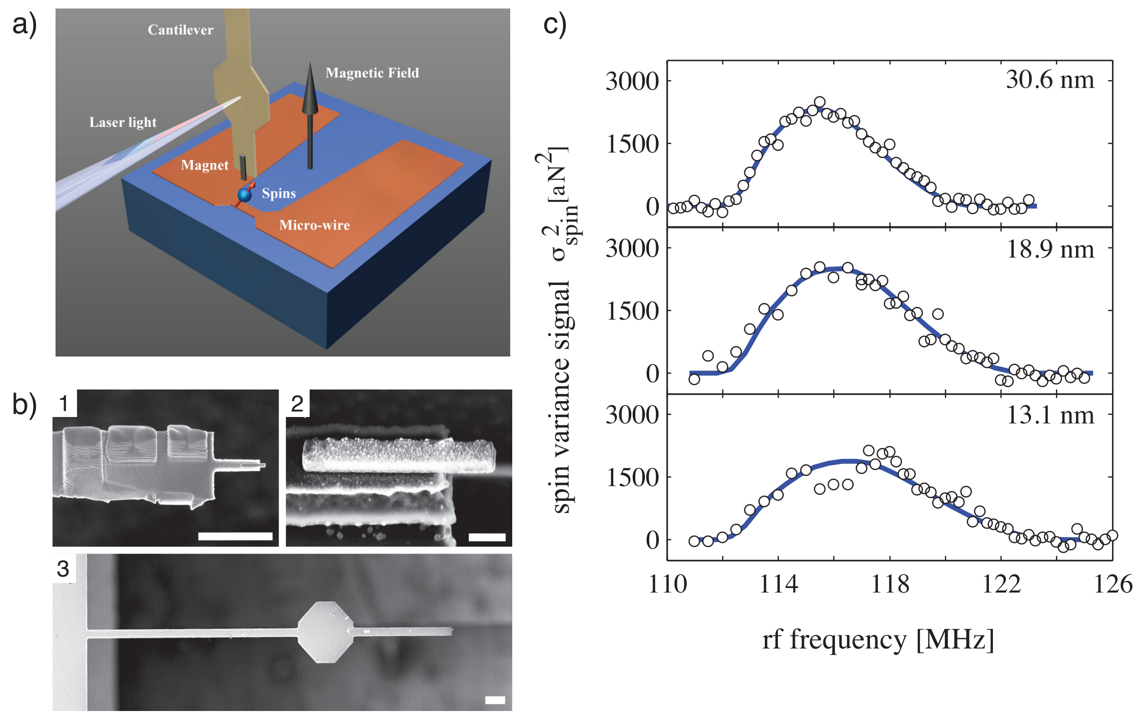

Figure 1: Cornell/IBM magnetic resonance force microscope NMR experiment. (a) Schematic of the experiment. (b) The magnet-tipped cantilever used in the experiment. 1. Top-view image of the magnet-tipped chip attached to an underlying cantilever by ion-assisted platinum deposition; three rectangular platinum adhesion patches can be seen on the top side of the chip. The overhanging cobalt magnet is attached to a 3 µm long finger at the leading edge of the chip. Scale bar = 5 µm. 2. Angled image of the overhanging cobalt nanomagnet, acquired before it was attached to a cantilever. The magnet is 225 ± 15 nm wide, 1494 ± 15 nm long, and 79 ± 4 nm thick. There is a 4 nm titanium layer under the magnet to promote adhesion to the silicon substrate, as well as an 8 nm platinum capping layer to mitigate oxidation. Scale bar = 200 nm. 3. Top-view image of a custom-fabricated 200 µm long cantilever, drawn from the same batch as the cantilever used in this experiment. Scale bar = 20 µm. (c) Magnetic resonance signal of protons in a 40 nm thick polystyrene film. Figure and caption adapted from Ref. 20.

necker and Marohn-group postdoc Lei Chen, and inserted into the IBM magnetic resonance force microscope. Proton magnetic resonance experiments were carried out by Mamin and Rugar in collaboration with the Cornell team. The cobalt-tipped cantilevers were used to detect stochastic proton magnetization from a polystyrene film spun-cast over a microwire.

See Fig. 1(a-b). The experiments employed a cobalt magnet with cross section $225\ \mathrm{nm}$ by $79\mathrm{nm}$; note how the magnet extends past the leading edge of the attonewton-sensitivity cantilever. The cantilever was centered over a $1\ \mu\mathrm{m}$-wide microwire coated with 40 nm of polystyrene. An external 2.63 T magnetic field was applied in the direction of the long axis of the cantilever as shown. A frequency-chirped rf waveform (peak-to-peak deviation 2 MHz) was applied to the microwire to cyclically invert the sample's proton magnetization at twice the mechanical resonance frequency f_c of the cantilever. The cantilever motion was measured with a laser interferometer. The interferometer output was sent to a lock-in amplifier that inferred the Fourier components of the cantilever oscillation moving in-phase and out-of-phase with the rf modulation. Because the sample's proton magnetization had a coherence time of ~ 0.1 s, the sample's magnetization interacting with the tip's magnetic field gradient led to spin-induced *force fluctuations* acting on the cantilever. A spin variance signal was obtained by comparing the variance of the cantilever displacement observed in the in-phase and out-of-phase lock-in channels.

The resulting spin variance signal, σ^2_{spin}, is plotted in Fig. 1(c) as a function of rf frequency at three tip-sample separations. The peak spin signal arises from a root-mean-square force of only 55 aN. The acquisition time was 12 to 17 minutes per data point. At this acquisition time the minimum detectable magnetic moment corresponds to approximately 500 fully polarized protons. The magnetic integrity of the tip at the nanoscale was assessed by comparing the spin signal to simulations carried out using different models of tip damage discussed below. The tip-field gradient calculated for the various tip models was $\partial B_z^{\text{tip}}/\partial z = 4.5$ to $5.4\,\text{MT m}^{-1}$.

The model which best described the data approximated the tip as fully magnetized with a 51 nm thick magnetically inactive layer at the leading edge. The simulated signal is shown as solid blue lines in Fig. 1(c); the agreement between experiment and simulation is excellent. The magnetic field gradient produced by our cobalt tip is 7.6 to 9.1-fold larger than the best tip gradient achieved in any previous magnet-on-cantilever MRFM experiment [24] — an extremely exciting advance. Moreover, our tip's gradient is comparable to the $4.2\,\text{MT m}^{-1}$ field gradient produced by the $Fe_{70}Co_{30}$ pillar in the sample-on-cantilever experiment of Ref. 25 in which 4 nm proton NMR imaging of a virus was demonstrated.

The 51 nm thickness of the magnetically inactive layer in the model is at odds with the ≤ 10 nm of oxidation observed in similarly aged Co thin-film control samples using depth-resolved XPS experiments. The apparent 51 nm thickness in the model therefore likely arises from a combination of oxidation, leading-edge roughness, and a protruding titanium adhesion layer. This observation suggests that reducing the titanium overhang and decreasing the grain size at the leading edge of the magnet will reduce the thickness of the apparent dead layer, give a larger tip-field gradient, and improve the spin sensitivity.

3.2.2 Understanding non-contact friction and frequency noise

When the MURI began, MRFM experiments had been carried out with attonewton-sensitivity cantilevers brought near a surface. In the most sensitive of these experiments it was recognized that force sensitivity was determined not by the intrinsic dissipation in the cantilever but by the extra dissipation arising from cantilever-surface interactions. Rugar and co-workers carried out measurements of dissipation over quartz and metal surfaces, showing that the surface dissipation arose from cantilever charges interacting with fluctuating electric field in the sample [17]; over a silicon sample the dissipation was shown to be proportional to the sample's doping level [26].

With partial support from the MURI and primary support from the NIH and NSF, Marohn's team carried out experimental and theoretical work to understand surface noise over polymer films [3–6]. A first-principles theory was developed for electric field and electric field gradient fluctuations over dielectrics, starting from the stochastic Maxwell equations of Lifshitz and using the sample's dielectric function as the only input [5]. This theory quantitatively explained the dependence of both dissipation and frequency noise as a function of function of polymer composition, film thickness, and tip-sample separation.

These studies were applicable to a cantilever operated in the "hangdown" geometry of Fig. 1(a). This reporting period, we extended our theory to encompass a cantilever vibrating normal to the sample surface [7] — the geometry used in some MRFM experiments [27–29] and in essentially all atomic force microscope experiments. This seemingly simple extension was surprisingly involved because now the tip charge is time dependent during a single cycle of the cantilever motion. We again observed excellent agreement between theory and experiment. These findings open the door to achieving quantitive dielectric-function image contrast in AFM *via* measurements of dissipation and frequency noise versus height and location.

This spring our theory collaborators, Professor Roger Loring and his group, succeeded after many years of effort in developing a theory for frequency noise over a molecular film containing mobile charges. This theory, again based on Maxwell's equations, treats exactly the interactions of the charges with each other and with dielectric fluctuations in the host material. The only inputs to the theory are the material's dielectric function, the charge density, and the charge's diffusion constant. The theory makes the remarkable prediction that charge-charge interactions suppress voltage fluctuations, and therefore cantilever frequency noise, by orders of magnitude over an organic transistor operated at typical charge densities (e.g., gate voltages). This prediction of suppressed noise was verified by experiment. A long paper describing these theoretical and experimental findings has been submitted to the *Journal of Chemical Physics* [8].

It must be kept in mind that the sample, and not the cantilever, has set the force sensitivity in the most sensitive MRFM experiments carried out to date. Taken together, our friction and frequency noise findings thus have important implications for designing high-sensitivity MRFM experiments.

Over dielectric films such as polymers and biopolymers, our work establishes that thermal dielectric fluctuations create attonewton-level force noise that can be predicted from first principles. In MRFM experiments the sample is often routinely coated with a metal film to shield the tip from the sample's electric field fluctuations. In our friction and frequency noise experiments, we find that some polymers such as polystyrene have even lower surface noise than gold. This finding suggests that, for some samples, gold-coating of samples is not necessarily the best practical strategy for obtaining low surface noise in an MRFM experiment. Our work indicates that, due to the long carrier screening length, charge-charge interactions in molecular conductors and semiconductors are effective at suppressing force noise and frequency noise. Thus, for "high noise" samples, a molecular conductor or semiconductor coating may be a preferable and lower-noise coating than a metal.

3.2.3 Spin detection protocols

Before the project began, we had invented a *force-gradient* method for observing magnetic resonance [30] — Cantilever Enabled Readout of Magnetization Inversion Transients or CERMIT [30; 31]. This spin-detection protocol has two unique capabilities. The first is that, in principle, it requires only one or a few spin flips to observe signal. This capability was recently exploited by Alexson and Smith at the U.S. Army Research Laboratory to measure the spin-lattice relaxation of ^{69}Ga magnetization at various temperatures [32] in a real-time single-shot inversion recovery experiment. This work was enabled by the MURI because the cantilevers for the experiment were produced by Hickman and Marohn at Cornell.

The second advantage of the CERMIT approach comes into play when it is used with cantilevers operating in close proximity to a surface. High-compliance, attonewton-sensitivity cantilevers must be operated in the "hangdown" geometry of Fig. 1(a) to avoid a destructive "snap in" to contact with the surface. In this geometry, force-based methods for detecting magnetic resonance can only observe a lateral spin imbalance in the sample, such as the imbalance created by magnetization fluctuations in small ensembles of spins. The second advantage of the CERMIT approach is that it enables the observation of both the mean spin polarization and polarization fluctuations.

With partial support from the MURI and primary support from the NIH and NSF, we have continued to evaluate spin-detection protocols.

During the reporting period we published a variant of the CERMIT approach that extends the applicability of force-gradient detection to spins having spin-lattice relaxation times T_1 as short as a single cantilever period of $\sim 200\ \mu$s [10]. This innovation made it possible for us to detect, at record sensitivity, electron spin resonance from the stable organic radical TEMPAMINE widely used in conventional-ESR studies of proteins and nucleic acids. This radical's short spin relaxation times ($T_1 = 1$ ms and $T_2 = 500$ ns) make it impossible to observe using the i-OSCAR force detection protocol employed by Rugar *et al.* to observe single-electron magnetic resonance *via* MRFM [9; 24].

Our new CERMIT experiment opens up a route for achieving single-electron detection of magnetic resonance in organic radicals at reasonably short averaging times. In the i-OSCAR experiment, the spin had a root-mean-square magnetization of $1\ \mu_B$; in a CERMIT experiment, one observes the mean (Curie law) spin magnetization which can be as high as $0.6\mu_B$ at 2.1 K and 2.1 T (e.g., at a 60 GHz resonance frequency). Although the magnitude of the signal in a single-spin CERMIT experiment is slightly smaller than in a single-spin i-OSCAR experiment, as discussed in Ref. 10 and shown below, the fact that the CERMIT experiment observes the mean spin polarization (which has a well defined sign) instead of polarization fluctuations (which have random sign) makes the signal-to-noise in the CERMIT experiment far more amenable to improvement by signal averaging.

A potential disadvantage of CERMIT detection is that the main source of noise is due to surface-induced frequency fluctuations, which are in general orders of magnitude larger than surface-induced force fluctuations. In this reporting period we demonstrated using non-degenerate parametric amplification to transform a slowly modulated force-gradient spin signal into a force signal oscillating on resonance with the cantilever [11]. This new detection paradigm has the advantages of both force detection (less susceptible to surface noise) and force-gradient detection (the ability to observe both the mean spin magnetization and magnetization fluctuations, potentially longer spin-coherence times during modulation, and lower rf duty cycle and thererfore less heating). We demonstrated the approach by evading surface frequency noise and detector noise in an MRFM measurement of ESR from TEMPAMINE.

In most prior theoretical treatments of the CERMIT effect, we assumed that the cantilever amplitude was much smaller than the diameter of the magnetic tip d and the tip-sample separation h [10; 11; 30; 33]. While this approximation has been valid in all CERMIT experiments carried out to date, optimizing the signal-to-noise ratio in a single-spin CERMIT experiment requires considering the case that the cantilever amplitude is comparable to d or h. We considered this limit in Ref. 33, but only for a single spin located directly below the tip. This reporting period we developed a formal description of frequency-shift MRFM experiments valid at any cantilever amplitude [34]. Remarkably, we were able to invent a single unified approach to numerically calculating signal from extended objects measured in both OSCAR and CERMIT experiments. The results of Ref. 34 will help us design and simulate optimal single-spin, as well as few-spin, measurements.

During the course of carrying out frequency-shift cantilever magnetometry experiments [21–23] to characterize the magnetization of individual nanomagnets on attonewton-sensitivity cantilevers, we discovered a new method for detecting nanoscale magnetic fields. This discovery was published during this reporting period [35]. In these experiments we applied a magnetic field oriented along the short axis of the nanomagnet tip — in the direction of the cantilever thickness in Fig. 1(b). Since the magnetization is oriented along the long axis of the nanomagnet at zero field, in this experiment we are observing a switching of the nanomagnet's magnetization from its magnetic easy axis to its magnetic hard axis. This kind of magnetization reorientation has only been observed once before in a cantilever magnetometry experiment [36], and never before with such a small magnetic tip and with such fine field steps. In our experiment we observed multiple distinct sharp transitions in cantilever frequency, dissipation, and frequency noise. These features, which we believe are due to switching of individual magnetic domains, are only a few gauss wide. The observed giant tip-induced changes in cantilever frequency and dissipation may thus represent a new route to detecting magnetic fields (and ultimately magnetic resonance) at nanoscale spatial resolution.

During this reporting period we also investigated using dynamic nuclear polarization (DNP) [37] to align nuclear spins in an MRFM experiment. Below we show that aligning nuclear spins by DNP could dramatically improve our ability to detect and image biomolecules at single proton sensitivity.

The experiment is sketched in Fig. 2(left). Experiments took place in vacuum, at a

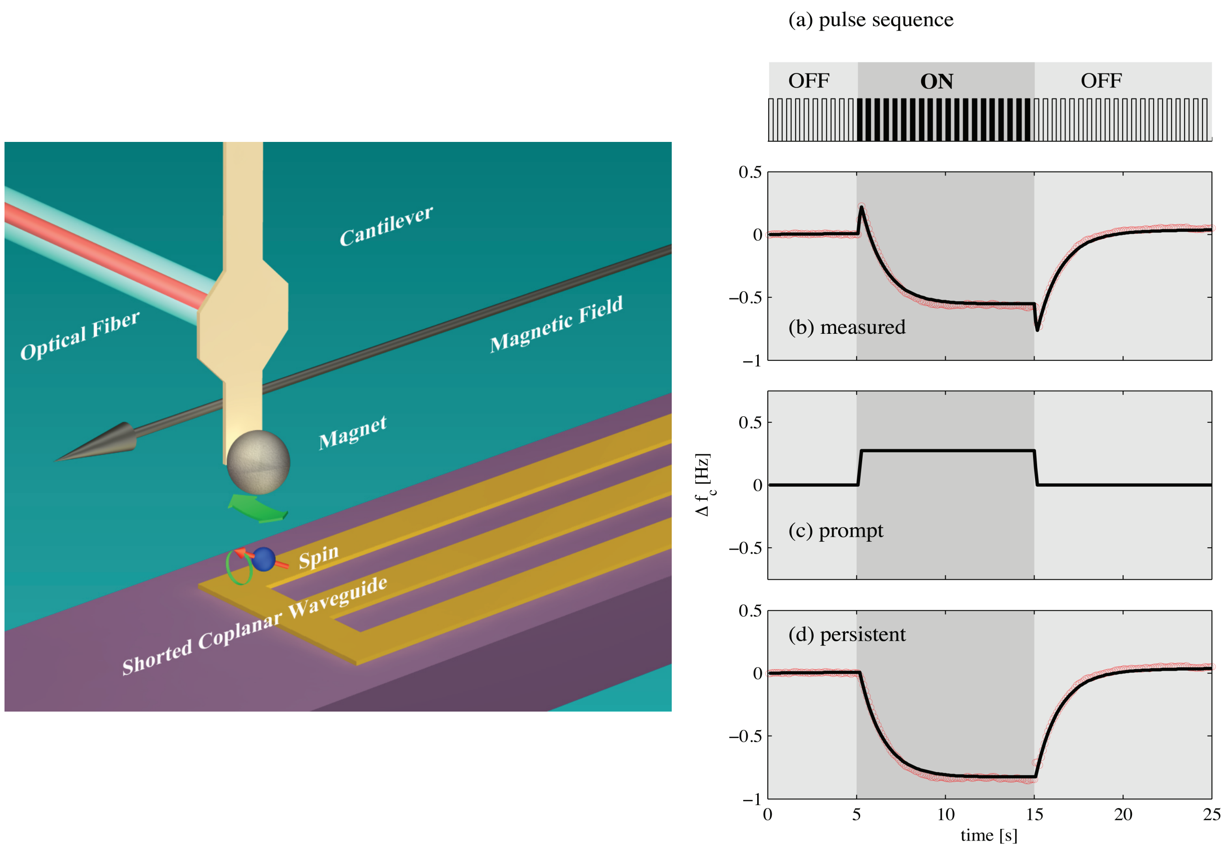

Figure 2: Scanned-probe dynamic nuclear polarization experiment. Left: Schematic drawing of the experimental setup. The drawing is not to scale. The black arrow represents the direction of the longitudinal polarizing magnetic field B_0. An artistically-rendered spin indicates the sample's electron spin magnetization, excited by the B_1. Right: (a) Microwave pulse sequence used to observe spin-induced transient changes in the cantilever's resonance frequency; the solid "ON" black bars indicate pulses in which the microwave frequency is *in resonance* with the applied magnetic field. The empty "OFF" bars indicate pulses in which the microwave frequency is *out of resonance* with the applied field. (b) The observed cantilever frequency shift as function of time (red circles) and fit to a piecewise sum of a square wave and an exponential rise and decay (solid line). Experimental parameters: cantilever amplitude $x_c = 131.7$ nm, tip-sample separation $h = 50$ nm, and static field $B_0 = 0.600$ T. (c) The *prompt*, square-wave best-fit component of the observed frequency shift due to saturated electron spins in the sample. (d) The prompt signal subtracted from the observed signal to yield the *persistent* signal (red circles). Also displayed is a best-fit to a rising and decaying exponential (solid line). Figure and caption adapted from Ref. 38.

temperature of $T = 4.2\,\mathrm{K}$, and in a background field centered at $B_0 = 0.6\,\mathrm{T}$ corresponding to an electron-spin resonance frequency of 18 GHz. A 200 nm thick film of perdeuterated polystyrene was doped with the free-radical TEMPAMINE at a concentration of 40 mM. An attonewton-sensitivity cantilever was prepared with a 4 micron diameter nickel tip and an optical fiber was aligned to the cantilever to watch its motion. The cantilever was brought in close proximity to a coplanar waveguide, which was shorted at the end to generate a large transverse microwave magnetic field B_1 (the broad arrow in Fig. 2(left)).

The cantilever was parked above the middle of one of the shorted segments. Changes in the sample magnetization were registered as a shift in the mechanical frequency of the cantilever [10].

The time sequence of applied microwaves and the resulting cantilever frequency shift are plotted in Figure 2(right). Microwaves were applied continuously and their frequency was switched essentially instantaneously from off-resonance to on-resonance. Because the applied power was constant, shifts in cantilever frequency induced by switching-related thermal transients were negligibly small. Upon shifting the microwave irradiation on resonance, the cantilever frequency exhibited a prompt, essentially instantaneous change due to saturation of the unpaired electron spins in the TEMPAMINE radical. Superimposed on this instantaneous frequency shift was a slower, persistent frequency shift. The risetime of the persistent shift was much longer than any thermal transient. As the applied field B_0 was scanned, the magnitude and sign of the persistent shift tracked the magnitude and sign of the prompt shift (data not shown). Because of its timescale, dependence on applied field B_0, magnitude, and exponential kinetics, we attribute the persistent shift to buildup of nuclear magnetization. A paper describing these findings has been submitted [38].

A persistent shift was not observed when the applied field was set in resonance with local spins directly below the tip; buildup was only observed when the static field was set in resonance with bulk spins far away from the tip. This finding indicates that buildup of dynamic nuclear polarization of deuterium may be suppressed by the large magnetic field gradient present directly below the tip. Harnessing dynamic nuclear polarization in an MRFM experiment may therefore require minimizing the magnetic field gradient experienced by the spins during DNP. We propose to achieve this in future experiments by shuttling the cantilever to the side during the DNP period.

3.2.4 Image Reconstruction Algorithms

We have focused on building models and algorithms for 3D MRFM image reconstruction when the point spread function is uncertain or only partially known. This problem is significant and our models and approaches have been strongly influenced by discussions with Dan Rugar.

During this period we have made significant progress, We published journal papers in *IEEE Trans. on Image Processing* in Sept. 2009 [39] and Sept. 2012 [40], and one other paper is in review at the same journal [41]. The 2009 journal paper introduced a hierarchical Bayesian method for 3D image reconstruction when the point spread function is known exactly. The method provides a comprehensive approach to MRFM reconstruction that incorporates physics models of the image formation process and, in addition to the image reconstruction, provides confidence intervals on the voxel intensities of the reconstructed image. Such confidence intervals are essential for doing hypothesis testing on reconstructed images, e.g. detecting an edge or shape of an object in the image, and were not available using standard Landweber methods used by Rugar. The method was applied to image reconstruction of the tobacco virus data collected by Rugar's group at

IBM.

The two other papers significantly extend the work described in the 2009 *IEEE* paper to the case where the point spread function is uncertain. The first paper reports on a MCMC approach to estimating simultaneously the point spread function and the image intensities, solving the so-called semi-blind reconstruction problem. The second paper introduces a variational Bayes approach that implements the semi-blind reconstruction approach of the first paper. This variational Bayes approach has significant computation advantages. Both semi-blind approaches come with confidence intervals on image intensities and on point spread function parameters.

In summary, we have developed a new and flexible class of MRFM image reconstruction methods. The advantages of these methods are the following. Unlike previous methods,

- the approach directly imposes natural sparsity models on the image,
- there are no sensitive tuning parameters to select,
- the reconstruction incorporates uncertainty on point spread response,
- the reconstruction algorithm outputs a full probability distribution of each pixel intensity,
- the performance of the algorithm can be monitored on the basis of this distribution, and
- the algorithm converges to the global maximum of the Bayesian risk function associated with mean square reconstruction error.

3.2.5 Spin Simulation Algorithms

Simulations play a central role in modern science and engineering, but it remains a challenge to simulate the large-scale, high-temperature, and nonequilibrium quantum systems that occur in applications such as magnetic resonance imaging, condensed matter, chemistry, and nanotechnology. Geometric descriptions of quantum trajectory unraveling lead to algorithms that can speed the computation of quantum simulations for broad classes of physical systems[1].

Simulation speed is enhanced whenever the rank-n matrix-vector products that generically appear in simulation equations are structured so as to be computed in $\mathcal{O}(n)$ operations, rather than the $\mathcal{O}(n^2)$ generally required. In recent years the resulting n-fold speedup has transformationally augmented the feasible scale of classical simulations.

During this reporting period we have been concerned with the question: Can a similar n-fold speedup be achieved in the simulation of quantum spin systems? We find that

[1]The text in this section is drawn nearly verbatim from Ref. 42

the answer is "yes." A long-established principle of of quantum system analysis simulation is that "a very large number of different physical viewpoints and widely different mathematical formulations that are all equivalent to one another." We have exploited this freedom to develop a quantum simulation framework that is closely similar to the symplectic mathematical framework of classical molecular dynamical simulation, and that simultaneously respects the orthodox principles of quantum mechanics, as these principles appear when translated onto symplectic state-spaces.

The central idea is to implement the orthodox equations of quantum simulation in such a way that simulated trajectories do not fill the entire Hilbert space, but rather are dynamically compressed onto a curved state-space of lower dimension, such that the curved state-space geometry describes the trajectory implicitly rather than explicitly. This is a familiar strategy in simulating classical systems by projective model order reduction (MOR), but it is less widely appreciated that this strategy is similarly effective in *quantum* simulations.

As an illustrative case we have simulated a generic dynamic nuclear polarization (DNP) process, in which spin polarization is transferred from a strongly polarized electron spin to an unpolarized nuclear spin.

It is characteristic of fields like biology and materials science that large ensembles of spins (or atoms, or electrons) are not the systems of interest, but rather investigations focus on nanoscale systems having a countable number of particles. In such cases the mean values of quantities like spin polarization can still be determined by taking time averages, but fluctuations in state-space processes and measurement processes are also observed. Therefore our framework encompasses the fluctuations in both the spin polarization and in a measurement process that continuously monitors that polarization, using algorithms that scale feasibly to the simulation of systems of hundreds, or potentially even thousands, of dynamical quantum spins.

3.3 Single proton detection outlook

In summary, our MURI team made tremendous advances in

- developing nanomagnet-tipped attonewton-sensitivity cantilevers,
- microscopically and spectroscopically quantifying the chemical composition of processed magnetic films and individual nanomagnets,
- understanding the force and force-gradient fluctuations experienced by an ultrasensitive cantilever near a surface,
- inventing spin-readout protocols that greatly extend the applicability of magnetic resonance force microscopy,
- inventing spin-readout protocols that evade surface frequency noise and detector noise,

- developing a new and flexible class of MRFM image reconstruction methods, and
- inventing and reducing to practice new approaches for simulating many coupled spins.

In addition, we have presented preliminary data suggesting, for the first time in an MRFM experiment,

- alignment of nuclear spins by transfer of polarization from electron spins.

Although we did not reach our goal of detecting single proton magnetic resonance, our MURI team's work has given us a very clear understanding of the remaining technical hurdles that need to be overcome to achieve single proton sensitivity. Moreover, our work suggests a clear technical path to this goal, which we describe in this section.

We begin by assessing the signal-to-noise of the Cornell/IBM experiment described above, and show that single proton sensitivity can be reached from this starting point *via* a combination of (1) challenging but achievable reductions in the thickness of the tip's magnetically inactive layer and (2) alignment of nuclear spins *via* transfer of polarization from electron spins.

We begin by calculating the signal-to-noise ratio for observing an individual proton using the Cornell/IBM experiment of Fig. 1. The signal-to-noise ratio for detecting magnetic resonance from a stochastically polarized single proton in a force-based magnetic resonance experiment is

$$\mathrm{SNR_P} = \frac{\mu_p^2\, G_{zx}^2}{S_F} \sqrt{T_{\text{avg}}\, \tau_m} \tag{1}$$

where $\mu_p = 1.41 \times 10^{-26}$ N m T^{-1} is the proton magnetic moment, $G_{zx} = \partial B_z^{tip}/\partial x$ is the lateral tip-field gradient, T_{avg} is the signal-averaging time, τ_m is the spin dephasing time during modulation, and S_F is the spectral density of force fluctuations experienced by the cantilever.

To estimate the gradient achievable with improved tips, is it convenient to model the tip as a uniformly magnetized sphere. The simplest tip model is shown in Fig. 3(a). To account for the magnetically inactive layer observed in all of our tips to date, we will use the tip model shown in Fig. 3(b). For comparison, the tip model used to analyze the data in Fig. 1 is shown in Fig. 3(c).

To magnetize the tip, a polarizing magnetic field is applied along the z axis in Fig. 3. We assume, for simplicity, that the magnitude of the polarizing field is larger than the tip field; in this case we only need to consider the z component of the tip field in the following calculations. The z component of the magnetic field outside of the uniformly magnetized sphere is

$$B_z^{\text{tip}} = B_s a^3 \left\{ \frac{3}{2}\frac{z^2}{r^5} - \frac{1}{2}\frac{1}{r^3} \right\} \tag{2}$$

with $r = \sqrt{x^2 + y^2 + z^2}$ the distance from the center of the sphere to the point of interest $\boldsymbol{r} = (x, y, z)$. Here $B_s = 2\mu_0 M_{\text{sat}}/3$ is the magnetic field at the north pole of the sphere,

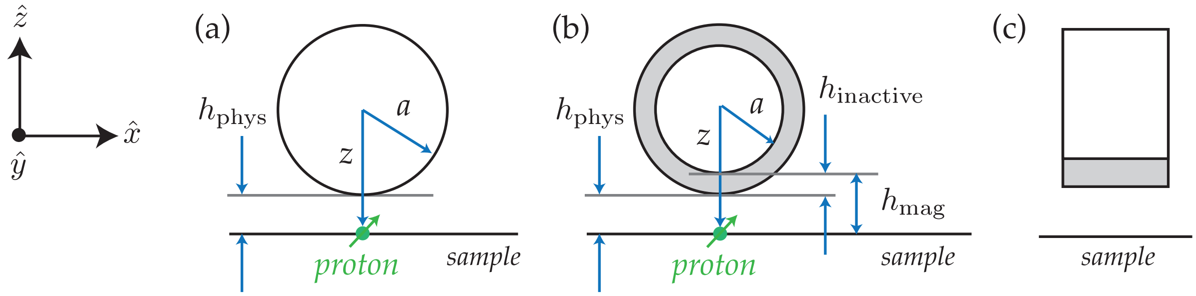

Figure 3: Tip models used to estimate the single-proton signal. (a) Spherical tip of radius a. The physical tip-sample separation is h_{phys}. A proton is located a vertical distance z from the center of the tip. (b) Spherical tip including a (shaded) magnetically inactive layer of thickness h_{inactive}. The effective magnetic spacing, the physical spacing plus the thickness of the inactive layer, is indicated as h_{mag}. (c) For comparison, the tip model is shown that was used to numerically simulate the spin variances in Fig. 1(c).

with M_{sat} the saturation magnetization and $\mu_0 = 4\pi \times 10^{-7}$ T m A^{-1} the permeability of free space. For cobalt, $\mu_0 M_{\text{sat}} = 1.8\,\text{T}$ and $B_s = 1.2\,\text{T}$.

We need to consider two field gradient components. The first is the vertical tip-field gradient $G_{zz} = \partial B_z^{\text{tip}}/\partial z$. Directly below the tip, $\boldsymbol{r} = (0, 0, z)$ and $G_{zz}(0, 0, z) = -3B_s a^3/z^4$, with $z = a + h_{\text{mag}}$ (Fig. 3(b)). At a fixed magnetic separation h_{mag}, the vertical gradient is maximized with a magnetic tip radius of $a^{\text{opt}} = 3\,h_{\text{mag}}$. The vertical gradient from this optimized magnetic tip is at a maximum directly below the tip and equal to

$$G_{zz}^{\text{opt}} = -0.316\,\frac{B_s}{h_{\text{mag}}}. \tag{3}$$

The second component to consider is the lateral tip-field gradient $G_{zx} = \partial B_z^{\text{tip}}/\partial x$. This gradient component determines the force on the sample spins; see Eq. 1 above and Eq. 5 below. For spins in an x, y plane located a distance $(0, 0, z)$ below the tip center, the lateral gradient component is maximized off to the side, at locations $x = \pm 0.389z$ and $y = 0$. Substituting $a = a^{\text{opt}} = 3\,h_{\text{mag}}$ gives the tip-optimized lateral field gradient at these locations as

$$G_{zx}^{\text{opt}} = \pm\,0.144\,\frac{B_s}{h_{\text{mag}}}. \tag{4}$$

By comparing Eq. 3 to Eq. 4, we see that for a spherical tip the tip-optimized lateral gradient off to the side is a factor of 0.457 smaller than the tip-optimized vertical gradient directly below the tip.

The spherical-tip model is a reasonably good representation of the real cuboid tip. From numerical models of the Fig. 1 signal we estimated the tip gradients in the Cornell/IBM experiment to be $G_{zz} = 4.4$ to 5.4 MT m^{-1} and $G_{zx} = 2.7$ to 8.3 MT m^{-1} at a tip-sample separation of $h_{\text{phys}} = 13.1$ nm. The lower bound is for a model assuming a cuboid tip have a leading-edge damage layer of $h_{\text{inactive}} = 51\,\text{nm}$ while the upper bound is for a model in which the tip has uniformly lower magnetization but no inactive layer. We model the tip as a sphere using $h_{\text{inactive}} = 51\,\text{nm}$ (Fig. 3(b)) and adjust the tip radius to give $G_{zz} = 5.4\,\text{MT m}^{-1}$. The resulting effective radius is $a = 120\,\text{nm}$, very close to the 133 nm geometric mean of the tip thickness (79 nm) and width (225 nm). The resulting G_{zx} is $2.5\,\text{MT m}^{-1}$, very close to the lateral tip-field gradient reported in Ref. 20. This agreement establishes that we can use the spherical tip model to estimate the improvement in lateral gradient obtainable by decreasing the thickness of the inactive layer.

We use Eq. 1 to calculate the signal-to-noise for detecting nuclear magnetic resonance from a stochastically polarized single proton using the magnet-on-cantilever Cornell/IBM experiment of Fig. 1 [20]. For consistency, we will use the gradient computed from the spherical-tip model. The result is

Case IA.	$G_{zx} = 2.5\,\text{MT m}^{-1}$
Cornell cantilever now	$S_F = (40\,\text{aN})^2\,\text{Hz}^{-1}$
Stochastic proton polarization	$\tau_m = 0.1\,\text{s}$
$\text{SNR}_\text{P} = 1.2 \times 10^{-4}$	$T_{\text{avg}} = 3\,\text{d}$

For comparison, for the high-frequency cantilever in the sample-on-cantilever experiment of Nichol, Budakian, and coworkers [43],

Case IB.	$G_{zx} = 0.12\,\text{MT m}^{-1}$
UIUC cantilever now	$S_F = (1.9\,\text{aN})^2\,\text{Hz}^{-1}$
Stochastic proton polarization	$\tau_m = 1.0\,\text{s}$
$\text{SNR}_\text{P} = 3.8 \times 10^{-4}$	$T_{\text{avg}} = 3\,\text{d}$

which is slightly better but SNR is still $\ll 1$. The silicon nanowire MRFM experiment of Ref. 43 had impressive force sensitivity, but their detection method requires a time-dependent gradient produced by running current through a wire and requires the sample to be affixed to the cantilever.

In the magnet-on-cantilever Cornell/IBM experiment we believe it is feasible to both increase the gradient and decrease the surface force noise. A tip similar to that shown Fig. 1(a) [1] experienced a spectral density of surface noise as good as $10\,\text{aN}\,\text{Hz}^{-1/2}$ down to tip-sample separations as small as $h = 3\,\text{nm}$ when operated over a gold-coated sample with the tip voltage adjusted to minimize the noise. Based on the known thermal oxidation layer thickness in cobalt, corroborated by our own XPS depth profiling studies of film oxidation and capping, we believe that reducing the thickness of the inactive layer to $h_{\text{inactive}} = 5\,\text{nm}$ will ultimately be possible. At a tip-sample separation of $h_{\text{phys}} = 10\,\text{nm}$ and $h_{\text{mag}} = 15$ nm, the optimal tip radius is $a^{opt} = 45$ nm, and the lateral gradient is $G_{zx} = 11.5\,\text{MT m}^{-1}$. Under these conditions,

Case IC.	$G_{zx} = 11.5\,\text{MT m}^{-1}$
Cornell cantilever improved	$S_F = (10\,\text{aN})^2\,\text{Hz}^{-1}$
Stochastic proton polarization	$\tau_m = 0.5\,\text{s}$
$\text{SNR}_\text{P} = 0.095$	$T_{\text{avg}} = 3\,\text{d}$

The signal to noise for the stochastically-polarized proton experiment, although significantly improved, is still well below 1. To obtain a signal-to-noise of $\mathrm{SNR_P} = 2.4$ would require $S_F = (2\,\mathrm{aN})^2\,\mathrm{Hz}^{-1}$, which has never been achieved with an audio-frequency cantilever near a surface. It is likewise difficult for us to see how to improve the gradient in the Ref. 43 experiment enough to obtain $\mathrm{SNR_P} > 1$ in reasonable averaging times.

Now let us examine how the signal-to-noise ratio improves by aligning the proton magnetization using DNP and detecting a coherent signal instead of an incoherent signal. The signal-to-noise ratio for detecting magnetic resonance from a coherent, well-aligned single proton in a force experiment is

$$\mathrm{SNR_A} = \frac{f_p\, \mu_p\, G}{\sqrt{S_F}} \sqrt{T_{\mathrm{avg}}} \tag{5}$$

with $f_p \leq 1$ the spin polarization of the individual proton and with G, μ_p, T_{avg}, and S_F defined as in Eq. 1. Here we assume, for simplicity, that the time to polarize the proton is shorter than the spin coherence time during detection; that is, we neglect any "deadtime" penalty associated with polarizing the proton magnetization. We expect this penalty to be small since both the DNP time and the spin coherence time during detection are thought to approach the nuclear spin's T_1 with strong rf and large frequency modulations.

In a DNP experiment the proton can in principle achieve a polarization f_p equal to the electron spin polarization f_e, given by

$$f_e = \tanh\left(\frac{\hbar \gamma_e B_0}{2 k_{\mathrm{B}} T}\right) \tag{6}$$

where $\hbar = 1.054 \times 10^{-34}$ J s^{-1} is Planck's constant, $\gamma_e = 1.76 \times 10^{11}$ rad s^{-1} T^{-1} is the gyromagnetic ration of the electron, $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant, B_0 is the applied field in tesla, and T is the temperature in kevin. In Fig. 4 we plot the electron spin polarization achievable at $T = 0.3$ K (a pumped ^{3}He refrigerator), $T = 2.1$ K (pumped ^{4}He), and $T = 4.2$ K (liquid helium) as functions of both magnetic field and the corresponding electron spin resonance frequency. At $T = 2.1$ K and $B_0 = 2.1$ T (e.g., 60 GHz), the calculated electron spin polarization is $p_e = 0.60$. Assuming perfectly efficient polarization transfer from electrons to protons, $f_p = 0.60$ also. Using the Cornell tip of Fig. 1, the signal-to-noise for detecting a coherent single proton would be

Case IIA.	$G_{zx} = 2.5\,\mathrm{MT\,m^{-1}}$
Cornell cantilever now	$S_F = (40\,\mathrm{aN})^2\,\mathrm{Hz}^{-1}$
Aligned proton polarization	$f_p = 0.60$
$\mathrm{SNR_A} = 0.27$	$T_{\mathrm{avg}} = 3$ d

which is a three order-of-magnitude improvement over the incoherent-spin force experiment of **Case IA**. Improving the force noise to the Hickman *et al*. value of $10\,\mathrm{aN\,Hz^{-1/2}}$ improves the signal-to-noise to $\mathrm{SNR_A} = 1.0$ — quite exciting. Interestingly, the estimated signal-to-noise for an analogous coherent single-proton experiment carried out the UIUC cantilever is similar:

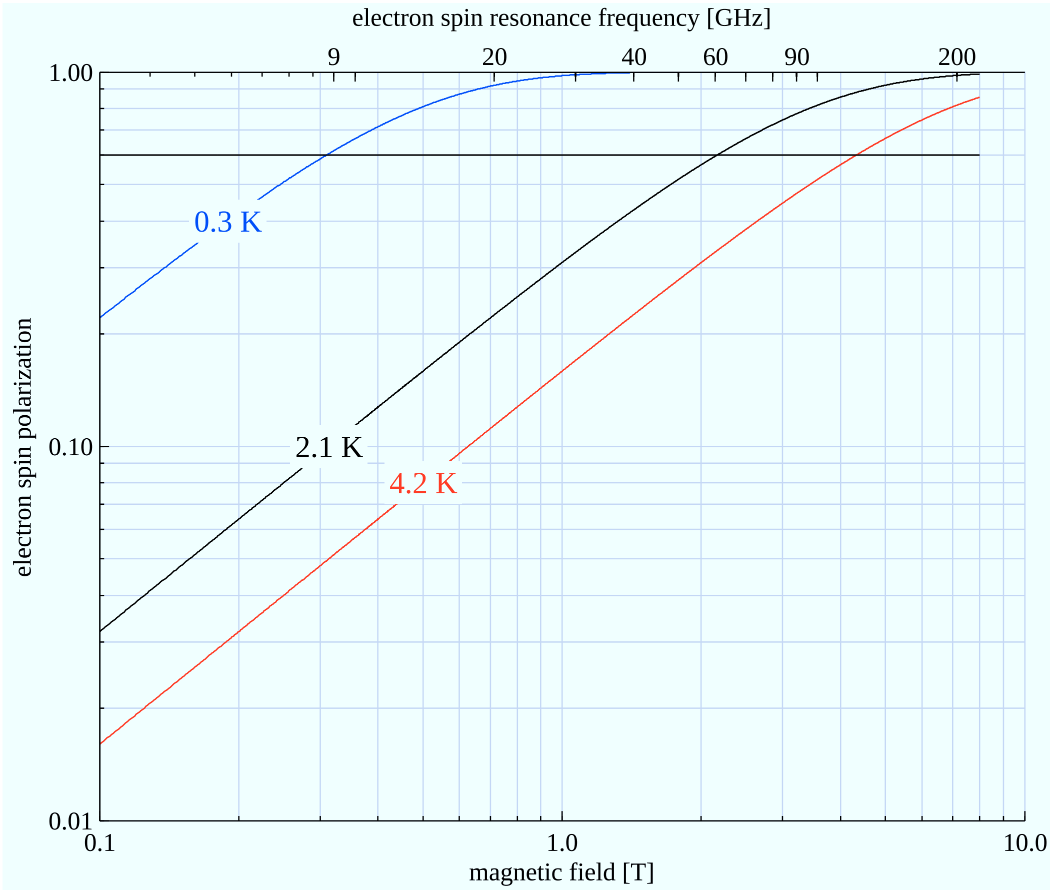

Figure 4: Electron spin polarization f_e, Eq. 6, versus applied magnetic field B_0 in tesla (lower axis). The corresponding electron spin resonance frequency $f_e = \gamma_e B_0/2\pi$ in GHz is shown on the upper axis. The electron spin polarization is shown at a temperature T of 4.2 K (red), 2.1 K (black), and 0.3 K (blue). The solid black horizontal line indicates an electron spin polarization of $p_e = 0.60$.

Case IIB.	$G_{zx} = 0.12\ \mathrm{MT\ m^{-1}}$
UIUC cantilever now	$S_F = (1.9\ \mathrm{aN})^2\ \mathrm{Hz^{-1}}$
Aligned proton polarization	$f_p = 0.60$
$\mathrm{SNR_A} = 0.26$	$T_{\mathrm{avg}} = 3\ \mathrm{d}$

As long as $f_p \geq 0.003 = 0.03\%$, the signal to noise for the coherent experiment exceeds that for the incoherent experiment. Assuming well-polarized protons in combination with the reduced noise and improved tip used in **Case IC** above, we calculate

Case IIC.	$G_{zx} = 11.5\ \mathrm{MT\ m^{-1}}$
Cornell cantilever improved	$S_F = (10\ \mathrm{aN})^2\ \mathrm{Hz^{-1}}$
Aligned proton polarization	$f_p = 0.60$
$\mathrm{SNR_A} = 4.95$	$T_{\mathrm{avg}} = 3\ \mathrm{d}$

Relaxing the signal averaging time to 1 day gives $\mathrm{SNR_A} = 2.85$ which is enough (assuming Gaussian noise) to identify more than 99% of protons in an individual molecule.

We believe the parameters used in the **Case IIC** calculation are challenging but achievable. Already we have evidence of $\leq 5\,\mathrm{nm}$ of surface damage in our best processed cobalt films, comparable to the thermal oxidation thickness. DNP at 30% efficiency is routine and DNP on the seconds timescale has been achieved in conventional magnetic resonance experiments [37], though not a temperatures as low as $2.1\,\mathrm{K}$.

3.4 Bibliography

[1] S. A. Hickman, E. W. Moore, S.-G. Lee, J. G. Longenecker, S. J. Wright, L. E. Harrell, and J. A. Marohn, Batch-fabrication of cantilevered magnets on attonewton-sensitivity mechanical oscillators for scanned-probe nanoscale magnetic resonance imaging, *ACS Nano*, **2010**, *4*, 7141 – 7150, [url].

[2] J. G. Longenecker, E. W. Moore, and J. A. Marohn, Rapid serial prototyping of magnet-tipped attonewton-sensitivity cantilevers by focused ion beam manipulation, *J. Vac. Sci. Technol. B*, **2011**, *29*, 032001, [url].

[3] S. Kuehn, R. F. Loring, and J. A. Marohn, Dielectric fluctuations and the origins of noncontact friction, *Phys. Rev. Lett.*, **2006**, *96*, 156103, [url].

[4] S. Kuehn, J. A. Marohn, and R. F. Loring, Noncontact dielectric friction, *J. Phys. Chem. B*, **2006**, *110*, 14525 – 145258, [url].

[5] S. M. Yazdanian, J. A. Marohn, and R. F. Loring, Dielectric fluctuations in force microscopy: Noncontact friction and frequency jitter, *J. Chem. Phys.*, **2008**, *128*, 224706, [url].

[6] S. M. Yazdanian, N. Hoepker, S. Kuehn, R. F. Loring, and J. A. Marohn, Quantifying electric field gradient fluctuations over polymers using ultrasensitive cantilevers, *Nano Lett.*, **2009**, *9*, 2273 – 2279, [url].

[7] N. Hoepker, S. Lekkala, R. F. Loring, and J. A. Marohn, Quantifying dielectric fluctuations over polymer films using an atomic force microscope, *J. Phys. Chem. B*, **2011**, *115*, 14493 – 14500, [url].

[8] S. Lekkala, N. Hoepker, J. A. Marohn, and R. F. Loring, Charge carrier dynamics and interactions in electric force microscopy, *J. Chem. Phys.*, **2012**, *137*, 124701, [url].

[9] D. Rugar, R. Budakian, H. J. Mamin, and B. W. Chui, Single spin detection by magnetic resonance force microscopy, *Nature*, **2004**, *430*, 329 – 332, [url].

[10] E. W. Moore, S.-G. Lee, S. A. Hickman, S. J. Wright, L. E. Harrell, P. P. Borbat, J. H. Freed, and J. A. Marohn, Scanned-probe detection of electron spin resonance from a nitroxide spin probe, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 22251 – 22256, [url].

[11] E. W. Moore, S.-G. Lee, S. A. Hickman, L. E. Harrell, and J. A. Marohn, Evading surface- and detector frequency noise in harmonic oscillator measurements of force gradients, *Appl. Phys. Lett.*, **2010**, *97*, 044105, [url].

[12] T. D. Stowe, K. Yasumura, T. W. Kenny, D. Botkin, K. Wago, and D. Rugar, Attonewton force detection using ultrathin silicon cantilevers, *Appl. Phys. Lett.*, **1997**, *71*, 288 – 290, [url].

[13] H. Mamin and D. Rugar, Sub-attonewton force detection at millikelvin temperatures, *Appl. Phys. Lett.*, **2001**, *79*, 3358 – 3360, [url].

[14] H. G. Craighead, Nanoelectromechanical systems, *Science*, **2000**, *290*, 1532 – 1535, [url].

[15] K. L. Ekinci and M. L. Roukes, Nanoelectromechanical systems, *Rev. Sci. Instrum.*, **2005**, *76*, 061101, [url].

[16] D. W. Carr, S. Evoy, L. Sekaric, H. G. Craighead, and J. M. Parpia, Measurement of mechanical resonance and losses in nanometer scale silicon wires, *Appl. Phys. Lett.*, **1999**, *75*, 920, [url].

[17] B. C. Stipe, H. J. Mamin, T. D. Stowe, T. W. Kenny, and D. Rugar, Noncontact friction and force fluctuations between closely spaced bodies, *Phys. Rev. Lett.*, **2001**, *87*, 096801, [url].

[18] N. E. Jenkins, L. P. DeFlores, J. Allen, T. N. Ng, S. R. Garner, S. Kuehn, J. M. Dawlaty, and J. A. Marohn, Batch fabrication and characterization of ultrasensitive cantilevers with submicron magnetic tips, *J. Vac. Sci. Technol. B*, **2004**, *22*, 909 – 915, [url].

[19] S. A. Hickman *Batch fabrication of cantilevered magnetic nanorods on attonewton-sensitivity silicon oscillators for magnetic resonance force microscopy* PhD thesis, Cornell University, Ithaca, New York, **2010**, [url].

[20] J. G. Longenecker, H. J. Mamin, A. W. Senko, L. Chen, C. T. Rettner, D. Rugar, and J. A. Marohn, High gradient nanomagnets on cantilevers for sensitive detection of nuclear magnetic resonance, *ACS Nano*, **2012**, *in press*, [url].

[21] J. A. Marohn, R. Fainchtein, and D. D. Smith, An optimal magnetic tip configuration for magnetic-resonance force microscopy of microscale buried features, *Appl. Phys. Lett.*, **1998**, *73*, 3778 – 3780, [url].

[22] B. C. Stipe, H. J. Mamin, T. D. Stowe, T. W. Kenny, and D. Rugar, Magnetic dissipation and fluctuations in individual nanomagnets measured by ultrasensitive cantilever magnetometry, *Phys. Rev. Lett.*, **2001**, *86*, 2874 – 2877, [url].

[23] T. N. Ng, N. E. Jenkins, and J. A. Marohn, Thermomagnetic fluctuations and hysteresis loops of magnetic cantilevers for magnetic resonance force microscopy, *IEEE Trans. Mag.*, **2006**, *42*, 378 – 381, [url].

[24] H. J. Mamin, R. Budakian, B. W. Chui, and D. Rugar, Detection and manipulation of statistical polarization in small spin ensembles, *Phys. Rev. Lett.*, **2003**, *91*, 207604, [url].

[25] C. L. Degen, M. Poggio, H. J. Mamin, C. T. Rettner, and D. Rugar, Nanoscale magnetic resonance imaging, *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, *106*, 1313 – 1317, [url].

[26] T. D. Stowe, T. W. Kenny, D. J. Thomson, and D. Rugar, Silicon dopant imaging by dissipation force microscopy, *Appl. Phys. Lett.*, **1999**, *75*, 2785 – 2787, [url].

[27] B. C. Stipe, H. J. Mamin, C. S. Yannoni, T. D. Stowe, T. W. Kenny, and D. Rugar, Electron spin relaxation near a micron-size ferromagnet, *Phys. Rev. Lett.*, **2001**, *87*, 277602, [url].

[28] I. Lee, Y. Obukhov, G. Xiang, A. Hauser, F. Yang, P. Banerjee, D. V. Pelekhov, and P. C. Hammel, Nanoscale scanning probe ferromagnetic resonance imaging using localized modes, *Nature*, **2010**, *466*, 845 – 848, [url].

[29] K. C. Fong, M. R. Herman, P. Banerjee, D. V. Pelekhov, and P. C. Hammel, Spin lifetime in small ensembles of electron spins measured by magnetic resonance force microscopy, *Phys. Rev. B*, **2011**, *84*, 220405, [url].

[30] S. R. Garner, S. Kuehn, J. M. Dawlaty, N. E. Jenkins, and J. A. Marohn, Force-gradient detected nuclear magnetic resonance, *Appl. Phys. Lett.*, **2004**, *84*, 5091 – 5093, [url].

[31] H. J. Mamin, M. Poggio, C. L. Degen, and D. Rugar, Nuclear magnetic resonance imaging with 90-nm resolution, *Nat. Nanotechnol.*, **2007**, *2*, 301 – 306, [url].

[32] D. A. Alexson, S. A. Hickman, J. A. Marohn, and D. D. Smith, Single-shot nuclear magnetization recovery curves with force-gradient detection, *Appl. Phys. Lett.*, **2012**, *101*, 022103, [url].

[33] S. Kuehn, S. A. Hickman, and J. A. Marohn, Advances in mechanical detection of magnetic resonance, *J. Chem. Phys.*, **2008**, *128*, 052208, [url].

[34] S.-G. Lee, E. W. Moore, and J. A. Marohn, A unified picture of cantilever frequency-shift measurements of magnetic resonance, *Phys. Rev. B*, **2012**, *85*, 165447, [url].

[35] S.-G. Lee, E. W. Moore, S. A. Hickman, J. G. Longenecker, and J. A. Marohn, Switching through intermediate states seen in a single nickel nanowire by cantilever magnetometry, *J. Appl. Phys.*, **2012**, *111*, 083911, [url].

[36] C. Miller, U. Mirsaidov, T. Messina, Y. Lee, and J. Markert, External field effects on the resonant frequency of magnetically capped oscillators for magnetic resonance force microscopy, *J. Appl. Phys.*, **2003**, *93*, 6572 – 6574, [url].

[37] R. G. Griffin and T. F. Prisner, High field dynamic nuclear polarization — the renaissance, *Phys. Chem. Chem. Phys.*, **2010**, *12*, 5737–5740, [url].

[38] L. Chen, J. G. Longenecker, E. W. Moore, and J. A. Marohn, Long-lived frequency shifts observed in a magnetic resonance force microscope experiment following microwave irradiation of a nitroxide spin probe, *Appl. Phys. Lett.*, **2012**, *in preparation*.

[39] N. Dobigeon, A. Hero, and J.-Y. Tourneret, Hierarchical bayesian sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2009**, *18*, 2059 – 2070, [url].

[40] S. U. Park, N. Dobigeon, and A. O. Hero, Semi-blind sparse image reconstruction with application to MRFM, *IEEE Trans. on Image Process.*, **2012**, *21*, 3838 – 3849, [url].

[41] S.-U. Park, N. Dobigeon, and A. O. Hero, Variational semi-blind sparse deconvolutionwith orthogonal kernel bases, *IEEE Trans. on Image Process.*, **2011**, *submitted*.

[42] J. A. Sidles, J. L. Garbini, J. P. Jacky, R. Picone, and S. Harsila, *Tutorial: Practical recipes for the simulation of large-scale open quantum systems*, Molecular Imaging 2009: Routes to Three-Dimensional Imaging of Single Molecules; Ithaca, New York; August 9 – 13, **2009**, [url].

[43] J. Nichol, E. Hemesath, L. Lauhon, and R. Budakian, Nanomechanical detection of nuclear magnetic resonance using a silicon nanowire oscillator, *Phys. Rev. B*, **2012**, *85*, 054414, [url].